

**THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Appellants: Senoo et al.  
Appl. No.: 09/162,992  
Conf. No.: 9466  
Filed: September 30, 1998  
Title: GEL ELECTRODE SECONDARY CELL  
Art Unit: 1795  
Examiner: Tracy Mae Dove  
Docket No.: 3712174-00037

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPELLANTS' APPEAL BRIEF**

Sir:

Appellants submit this Appeal Brief in support of the Notice of Appeal filed on October 4, 2010. This Appeal is taken from the Final Rejection dated July 2, 2010 and the Notice of Panel Decision from Pre-Appeal Brief Review dated October 20, 2010.

**I. REAL PARTY IN INTEREST**

The real party in interest for the above-identified patent application on Appeal is Sony Corporation by virtue of Assignments dated November 20, 1998, November 24, 1998, November 26, 1998 and November 30, 1998 and recorded at reel 009622, frame 0510 in the United States Patent and Trademark Office.

## **II. RELATED APPEALS AND INTERFERENCES**

Appellants' legal representative and the Assignee of the above-identified patent application do not know of any prior or pending appeals, interferences or judicial proceedings which may be related to, directly affect or be directly affected by or have a bearing on the Board's decision with respect to the above-identified Appeal.

### **III. STATUS OF CLAIMS**

Claims 26-32 and 35-39 are pending in the above-identified patent application. Claims 1-25 and 33-34 were previously canceled without prejudice or disclaimer. Claims 26-32 and 35-39 stand rejected. Therefore, Claims 26-32 and 35-39 are being appealed in this Brief. A copy of the appealed claims is included in the Claims Appendix.

#### **IV. STATUS OF AMENDMENTS**

A non-final Office Action was mailed on January 15, 2010, in which the Examiner rejected Claim 39 under 35 U.S.C. §112, first paragraph, Claims 26-32 and 34-39 under 35 U.S.C. §112, second paragraph, and Claims 26-32 and 34-39 under 35 U.S.C. §103. Appellants filed a Response to the non-final Office Action on February 2, 2010, in which Appellants canceled Claim 34, amended Claims 26 and 39, and argued against the written description, indefiniteness and obviousness rejections. A final Office Action was mailed on July 2, 2010, in which the Examiner rejected Claim 39 under 35 U.S.C. §112, second paragraph, and maintained its rejections of Claims 26-32 and 34-39 under 35 U.S.C. §103. Appellants filed a Notice of Appeal and Pre-Appeal Brief in response to the final Office Action on October 4, 2010, in which Appellants argued against the indefiniteness and obviousness rejections. The Patent Office issued a Notice of Panel Decision from Pre-Appeal Brief Review on October 20, 2010 maintaining its indefiniteness and obviousness rejections. Copies of the non-final Office Action, final Office Action and Notice of Panel Decision from Pre-Appeal Brief Review are included in the Evidence Appendix as Exhibits A, B and C, respectively.

## V. SUMMARY OF CLAIMED SUBJECT MATTER

A summary of the invention by way of reference to the specification and/or figures for each of the independent claims is provided as follows:

Claim 26 is directed to a gel electrolyte secondary cell (page 1, paragraphs 2, 15 and 17-18; page 2, paragraphs 26-28, 30 and 32; page 3, paragraphs 42 and 49; page 4, paragraphs 52-58 and 60; pages 4-5, paragraph 67; page 5, paragraphs 68 and 80; page 6, paragraphs 86 and 94) comprising: a positive electrode (page 1, paragraph 10; page 2, paragraphs 23, 27 and 32; page 3, paragraphs 42 and 44-48; page 4, paragraphs 58-59; page 5, paragraph 80; page 6, paragraphs 84-86); a negative electrode (page 1, paragraph 10; page 2, paragraphs 23-24, 27, 30 and 32) comprising a current collector (page 2, paragraph 23; page 3, paragraphs 36, 39, 41 and 46-48; page 4, paragraph 64; page 6, paragraphs 83, 85 and 90) and a powder mixture composed of a graphite material (page 2, paragraphs 28-30 and 32-33; page 3, paragraphs 35-37, 40 and 42-43; page 5, paragraphs 73-75, 77-79 and 82; page 6, paragraphs 84, 87 and 92-94) having a mean particle size of 5 to 100  $\mu\text{m}$  (page 3, paragraph 37); and a gel electrolyte (page 1, paragraphs 2, 15 and 17-19; page 2, paragraphs 20, 22-28, 30 and 32; page 3, paragraphs 37, 42-44 and 49; page 4, paragraphs 52, 54-57 and 60; pages 4-5, paragraph 67; page 5, paragraph 80; page 6, paragraphs 86 and 94) comprising an electrolyte salt (page 1, paragraph 13; page 3, paragraphs 49-50; pages 3-4, paragraph 51; page 4, paragraphs 54-55), a non-aqueous solvent (page 1, paragraphs 12 and 19; page 3, paragraphs 49-50; pages 3-4, paragraph 51; page 4, paragraphs 52 and 54-55; pages 4-5, paragraph 67) and a high-molecular weight material (page 1, paragraph 18; page 3, paragraph 49; page 4, paragraphs 53-55; pages 4-5, paragraph 67), wherein the non-aqueous solvent comprises propylene carbonate (page 1, paragraphs 12 and 18-19; page 2, paragraphs 20-21, 25 and 28; page 3, paragraph 43; page 4, paragraphs 52 and 57; pages 4-5, paragraph 67; page 6, paragraph 94) and ethylene carbonate (page 1, paragraph 12; page 4, paragraphs 52 and 57; pages 4-5, paragraph 67), wherein a content of propylene carbonate ranges from 10 mol% to 75 mol% (page 4, paragraph 52; pages 4-5, paragraph 67), and wherein the graphite material is obtained by sintering meso-carbon micro-beads (Abstract; page 2, paragraphs 27-34; page 3, paragraph 35; page 4, paragraph 62; page 5, paragraphs 69, 73, 78-79 and 82; page 6, paragraphs 92-94).

Although specification citations are given in accordance with C.F.R. 1.192(c), these reference numerals and citations are merely examples of where support may be found in the specification for the terms used in this section of the Brief. There is no intention to suggest in any way that the terms of the claims are limited to the examples in the specification. As demonstrated by the references numerals and citations below, the claims are fully supported by the specification as required by law. However, it is improper under the law to read limitations from the specification into the claims. Pointing out specification support for the claim terminology as is done here to comply with rule 1.192(c) does not in any way limit the scope of the claims to those examples from which they find support. Nor does this exercise provide a mechanism for circumventing the law precluding reading limitations into the claims from the specification. In short, the references numerals and specification citations are not to be construed as claim limitations or in any way used to limit the scope of the claims.

## VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1. Claim 39 is rejected under 35 U.S.C. §112, second paragraph, as being indefinite.
2. Claims 26-32 and 35-39 are rejected under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 5,772,934 to MacFadden ("*MacFadden*") in view of U.S. Patent No. 6,280,878 B1 to Maruyama et al. ("*Maruyama*"). Copies of *MacFadden* and *Maruyama* are included in the Evidence Appendix as Exhibits D and E, respectively.
3. Claims 26-32 and 35-39 are rejected under 35 U.S.C. §103(a) as being unpatentable over *MacFadden* in view of U.S. Patent No. 5,522,127 to Ozaki et al. ("*Ozaki*"). A copy of *Ozaki* is included in the Evidence Appendix as Exhibit F.
4. Claims 26-32 and 35-39 are rejected under 35 U.S.C. §103(a) as being unpatentable over European Patent No. 0724305 B1 to Akashi ("*Akashi*") in view of *Ozaki*. A copy of *Akashi* is included in the Evidence Appendix as Exhibit G.



## VII. ARGUMENT

### A. LEGAL STANDARDS

#### 1. Definiteness under 35 U.S.C. §112, second paragraph

The standard for determining whether the definiteness requirement is met under 35 U.S.C. § 112, ¶ 2 is “whether those skilled in the art would understand what is claimed when the claim is read in light of the Specification.” *Orthokinetics Inc. v. Safety Travel Chairs Inc.*, 1 U.S.P.Q. 2d 1081-1088 (Fed. Cir. 1986). “If the claims, read in light of the Specification, reasonably apprise those skilled in the art both of the utilization and scope of the invention, and if the language is as precise as the subject matter permits, the Courts can demand no more.” *North American Vaccine Inc. v American Cyanamid Co.*, 28 U.S.P.Q. 2d 1333, 1339 (Fed. Cir. 1993). In this regard, “[p]atent law allows the inventor to be his own lexicographer ... [T]he specification aids in ascertaining the scope and meaning of the language employed in the claims inasmuch as words must be used in the same way in both the claims and the specification. *United States v. Teletronics, Inc.*, 8 U.S.P.Q. 2d 1217, 1220 (Fed. Cir. 1988). By statute, 35 U.S.C. 112, Congress has placed no limitations on how an applicant claims his invention, so long as the specification concludes with claims which particularly point out and distinctly claim that invention.” *In re Pilkington*, 162 U.S.P.Q. 145, 148 (C.C.P.A. 1996).

#### 2. Obviousness under 35 U.S.C. § 103

The Federal Circuit has held that the legal determination of an obviousness rejection under 35 U.S.C. § 103 is:

whether the claimed invention as a whole would have been obvious to a person of ordinary skill in the art at the time the invention was made...The foundational facts for the prima facie case of obviousness are: (1) the scope and content of the prior art; (2) the difference between the prior art and the claimed invention; and (3) the level of ordinary skill in the art...Moreover, objective indicia such as commercial success and long felt need are relevant to the determination of obviousness...Thus, each obviousness determination rests on its own facts.

*In re Mayne*, 41 U.S.P.Q. 2d 1451, 1453 (Fed. Cir. 1997).

In making this determination, the Patent Office has the initial burden of proving a *prima facie* case of obviousness. *In re Rijckaert*, 28 U.S.P.Q. 2d 1955, 1956 (Fed. Cir. 1993). This burden may only be overcome “by showing some objective teaching in the prior art or that knowledge generally available to one of ordinary skill in the art would lead that individual to combine the relevant teachings.” *In re Fine*, 5 U.S.P.Q. 2d 1596, 1598 (Fed. Cir. 1988). “If the examination at the initial stage does not produce a *prima facie* case of unpatentability, then without more the applicant is entitled to grant of the patent.” *In re Oetiker*, 24 U.S.P.Q. 2d 1443, 1444 (Fed. Cir. 1992).

Moreover, the Patent Office must provide explicit reasons why the claimed invention is obvious in view of the prior art. The Supreme Court has emphasized that when formulating a rejection under 35 U.S.C. § 103(a) based upon a combination of prior art elements it remains necessary to identify the reason why a person of ordinary skill in the art would have combined the prior art elements in the manner claimed. *KSR v. Teleflex*, 127 S. Ct. 1727 (2007).

Of course, references must be considered as a whole and those portions teaching against or away from the claimed invention must be considered. *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve Inc.*, 796 F.2d 443 (Fed. Cir. 1986). “A prior art reference may be considered to teach away when a person of ordinary skill, upon reading the reference would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the Applicant.” *Monarch Knitting Machinery Corp. v. Fukuhara Industrial Trading Co., Ltd.*, 139 F.3d 1009 (Fed. Cir. 1998), quoting, *In re Gurley*, 27 F.3d 551 (Fed. Cir. 1994).

## B. THE CLAIMED INVENTION

Claim 1 is directed to a gel electrolyte secondary cell. The cell includes a positive electrode, a negative electrode and a gel electrolyte. The negative electrode comprises a current collector and a powder mixture composed of a graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ . The gel electrolyte comprises an electrolyte salt, a non-aqueous solvent and a high-molecular weight material. The non-aqueous solvent comprises propylene carbonate and ethylene carbonate, and a content of propylene carbonate ranges from 10 mol% to 75 mol%. The graphite material is obtained by sintering meso-carbon micro-beads.

C. CLAIM 26 IS SUFFICIENTLY DEFINITE TO SATISFY THE REQUIREMENTS UNDER 35 U.S.C. §112, SECOND PARAGRAPH

The standard for determining whether the definitiveness requirement is met under 35 U.S.C. §112, second paragraph, is whether those skilled in the art would understand what is claimed when the claim is read in light of the specification. The Examiner asserts that the phrase “obtained by directly firing” lacks antecedent basis because claim 26 recites a material “obtained by sintering.” See, Final Office Action, page 2, lines 15-22. Appellants respectfully disagree with the Examiner and submit that, when read in light of the specification, claim 39 requires that the sintering of the meso-carbon micro-beads (to obtain the graphite material as defined in independent claim 26) is achieved by directly firing the meso-carbon micro-beads at a temperature between 2500° C and 3500° C. For example, the Specification discloses obtaining its graphite material by firing meso-carbon micro-beads at an elevated temperature. See, Specification, page 3, paragraph 35. Example 1 in the Specification teaches a negative electrode including “a fired material of meso-carbon micro-beads.” See, Specification, page 4, paragraph 62. Example 3 discloses a negative electrode comprised of “sintered meso-carbon micro-beads. . . prepared in the same way as in Example 1.” See, Specification, page 5, paragraph 82. One of ordinary skill in the art would thus understand that the terms “sintering” and “firing” are synonymous. Therefore, claim 39 should be deemed to have proper antecedent basis.

D. THE REJECTION OF CLAIMS 26-32 AND 35-39 UNDER 35 U.S.C. §103(a) TO MACFADDEN AND MARUYAMA SHOULD BE REVERSED BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS

Appellants respectfully submit that the obviousness rejection of Claims 26-32 and 35-39 should be reversed because the Examiner has failed to establish a *prima facie* case of obviousness. In the final Office Action, the Examiner asserts that the combination of *MacFadden* and *Maruyama* renders the claimed subject matter obvious. See, Final Office Action, pages 3-11. However, the Examiner has failed to establish a *prima facie* case of obviousness because, even if combinable, the cited references fail to disclose each and every element of the present claims.

1. The Cited References Fail to Disclose Each and Every Element of the Present Claims

Independent Claim 1 recites, in part, a gel electrolyte secondary cell comprising: a positive electrode; a negative electrode comprising a current collector and a powder mixture composed of a graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ ; and a gel electrolyte comprising an electrolyte salt, a non-aqueous solvent and a high-molecular weight material, wherein the non-aqueous solvent comprises propylene carbonate and ethylene carbonate, wherein a content of propylene carbonate ranges from 10 mol% to 75 mol%, and wherein the graphite material is obtained by sintering meso-carbon micro-beads. In conventional non-aqueous electrolyte cells using graphite as a negative electrode and propylene carbonate as a non-aqueous solvent, propylene is generally decomposed due to the instability of propylene carbonate against conventional graphite materials, thereby lowering the charge/discharge efficiency. See, Specification, page 2, paragraph 20. However, by providing propylene carbonate in combination with the claimed graphite material, an improved charge/discharge efficiency can be obtained. See, Specification, pages 4-5, paragraph 67; page 5, paragraphs 68-69 and 82; page 6, paragraphs 87-88; Tables 1-2. In contrast, Appellants respectfully submit that the cited references are deficient with respect to the present claims.

Appellants respectfully submit that, even if combinable, the combination of *MacFadden* and *Maruyama* fails to disclose or suggest a gel electrolyte secondary cell including a negative electrode comprising a powder mixture composed of a graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ , wherein the graphite material is obtained by sintering meso-carbon micro-beads as recited, in part, by independent Claim 26. The Examiner admits that *MacFadden* is silent regarding the mean particle size of the graphite material and instead relies on *Maruyama* for the claimed graphite material. See, Final Office Action, page 5, lines 3-15. However, nowhere does *Maruyama* teach or suggest that its graphite is obtained by sintering meso-carbon micro-beads, nor does the Examiner cite support for such claimed element. Instead, the Examiner asserts that the limitation in Claim 26 that the graphite material is “obtained by sintering meso-carbon micro-beads” is a product-by-process claim which should not be given patentable weight “in the absence of unexpected results.” See, Final Office Action, page 2, lines 6-9.

Appellants respectfully disagree with the Examiner's refusal to give the limitation "wherein the graphite material is obtained by sintering meso-carbon micro-beads" patentable weight. The Federal Circuit recently stated that "process terms that define the product in a product-by-process claim serve as enforceable limitations." *Abbott Labs. v. Sandoz, Inc.*, 566 F.3d 1282 (Fed. Cir. 2009). The Court further explained that "if an inventor invents a product whose structure is either not fully known or too complex to analyze. . . this court clarifies that the inventor is absolutely free to use process steps to define this product." *Id.* Appellants respectfully submit that product-by-process limitations may be used to define a product and, thus, the limitation that "the graphite material is obtained by sintering meso-carbon micro-beads" should be given patentable weight.

Moreover, Appellants respectfully disagree with the Examiner's requirement that the claimed product demonstrate unexpected results. The appropriate standard in determining whether a product-by-process claim is valid is not whether there are unexpected results but whether the resulting product is new and not obvious. *Amgen Inc. v. F. Hoffman-La Roche Ltd.*, 580 F.3d 1340 (Fed. Cir. 2009). For example, the Court found that recombinant EPO "purified from mammalian cells grown in culture" was distinguishable from urinary EPO because studies indicated that recombinant EPO had a higher molecular weight and different charge than urinary EPO due to differences in carbohydrate composition. *Id.* Similarly, a gel electrolyte secondary cell including the claimed graphite exhibits different properties, such as a higher charging/discharging efficiency, than a gel electrolyte secondary cell including graphite obtained by other means such as firing coke. See, Specification, page 5, paragraphs 78-79; page 6, paragraphs 92-93; Tables 1-2. Thus, the Specification adequately demonstrates that a graphite material obtained by sintering meso-carbon micro-beads is distinguishable from other graphite materials.

Even if the Examiner's standard of unexpected results is applied, the gel electrolyte secondary cell including the specific graphite material as claimed is not anticipated by or obvious over the graphite material of *Maruyama*. For example, Table 1 demonstrates initial charging/discharging efficiencies of 82.8% and 82.6% in a gel electrolyte cell when a graphite material obtained by sintering meso-carbon micro-beads is used as the anode material, whereas a significantly lower efficiency of only 61% is achieved in a gel electrolyte cell that is the entirely the same except for using a graphite material obtained by firing petroleum coke. See,

Specification, page 4, paragraph 62; page 5, paragraphs 69, 71-72 and 77-78; Table 1. Similarly, Table 2 demonstrates initial charging/discharging efficiencies of 74.5% and 74.1% in a gel electrolyte cell when a graphite material obtained by sintering meso-carbon micro-beads is used as the anode material, whereas a significantly lower efficiency of only 56% is achieved in a gel electrolyte cell that is the entirely the same except for using a graphite material obtained by firing petroleum coke. See, Specification, page 5, paragraph 82; page 6, paragraphs 87-88 and 91-93; Table 2.

The Examiner asserts that Tables 1 and 2 do not show evidence of unexpected results because they do not distinguish the claimed material over the prior art of record. See, Final Office Action, page 10, lines 5-9. However, *Maruyama* merely discloses that “[t]he carbon used as the active material may be properly selected from natural or artificial graphite, resin fired carbon materials, and carbon fibers. . . . Preferred among these is graphite desirably having a mean particle size of 1 to 30  $\mu\text{m}$ .” See, *Maruyama*, column 5, lines 9-13. Nowhere does *Maruyama* recognize any importance in how its graphite is formed or teach forming its graphite in any specific manner. As discussed previously, the Specification demonstrates unexpected results when a graphite material obtained by sintering meso-carbon micro-beads is used versus other graphite materials. See, Specification, Tables 1-2. As such, Appellants respectfully submit that the cited references fail to disclose or suggest each and every element of the present claims.

Accordingly, Appellants respectfully request that the rejection of Claims 26-32 and 35-39 under 35 U.S.C. §103(a) to *MacFadden* and *Maruyama* be reconsidered and withdrawn.

D. THE REJECTION OF CLAIMS 26-32 AND 35-39 UNDER 35 U.S.C. §103(a) TO *MACFADDEN* AND *OZAKI* SHOULD BE REVERSED BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS

Appellants respectfully submit that the obviousness rejection of Claims 26-32 and 35-39 should be reversed because the Examiner has failed to establish a *prima facie* case of obviousness. In the final Office Action, the Examiner asserts that the combination of *MacFadden* and *Ozaki* renders the claimed subject matter obvious. See, Final Office Action, pages 3-11. However, the Examiner has failed to establish a *prima facie* case of obviousness because, there exists no reason why the skilled artisan would have combined *MacFadden* and *Ozaki* to arrive at the presently claimed subject matter.

1. The Skilled Artisan Would Have No Reason to Combine the Cited References to Arrive at the Present Claims

Appellants respectfully submit that one of ordinary skill in the art would have no reason to combine the mesophase carbon micro beads of *Ozaki* with the propylene carbonate solvent of *MacFadden* to arrive at the present claims because *Ozaki* teaches away from using its micro beads with propylene carbonate. References must be considered as a whole and those portions teaching against or away from each other and/or the claimed invention must be considered. *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve Inc.*, 796 F.2d 443 (Fed. Cir. 1986). “A prior art reference may be considered to teach away when a person of ordinary skill, upon reading the reference would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the Applicant.” *Monarch Knitting Machinery Corp. v. Fukuhara Industrial Trading Co., Ltd.*, 139 F.3d 1009 (Fed. Cir. 1998), quoting, *In re Gurley*, 27 F.3d 551 (Fed. Cir. 1994).

The Examiner asserts that “[o]ne of skill would have been motivated to use the graphite negative electrode of *Ozaki* as the graphite negative electrode of *MacFadden* because both materials are capable of intercalating lithium and the graphite negative electrode of *Ozaki* leads to increased cell capacity.” See, Office Action, page 7, lines 5-8. However, Appellants respectfully submit that one of ordinary skill in the art would have no reason to substitute the graphite particles of *Ozaki* for the graphite particles of *MacFadden* because *Ozaki* teaches away from using its graphite particles with a propylene carbonate solvent such as that contained in the cell of *MacFadden*. For example, *Ozaki* expressly teaches that propylene carbonate is not suitable for use with its mesophase graphite particles:

As for the organic solvent of the organic electrolyte for the non-aqueous electrolyte, propylene carbonate (PC) is not employed, because it decomposes to generate a gas [at] during charging. On the other hand, ethylene carbonate (EC) used alone is not suitable, since it has a high melting temperature and is solid at ordinary temperature, though it has no unfavorable side reaction, as of PC. However, EC may be used in a mixed solvent of EC and either ether such as 1,2 dimethoxyethane, chain carbonate such as diethyl carbonate, ethyl methyl carbonate, or aliphatic-carboxylic acid ester such as methyl propionate, which are of low melting temperature and of low viscosity.

See, *Ozaki*, column 7, lines 5-16. *Ozaki*'s teaching that propylene carbonate has unfavorable side reactions with its graphite particles would have discouraged one of ordinary skill in the art from combining meso-carbon micro-beads with propylene carbonate in accordance with the present claims.

Appellants submit that it would also not have been obvious to combine the mesophase carbon micro beads of *Ozaki* with the propylene carbonate solvent of *MacFadden* to arrive at the present claims the Specification demonstrates unexpected results when combining propylene carbonate with graphite obtained by firing meso-carbon micro beads. For example, Table 1 demonstrates initial charging/discharging efficiencies of 82.8% and 82.6% in a gel electrolyte cell containing propylene carbonate when a graphite material obtained by sintering meso-carbon micro-beads is used as the anode material, whereas a significantly lower efficiency of only 61% is achieved in the same gel electrolyte cell when the anode material is substituted with a graphite material obtained by firing petroleum coke. See, Specification, page 4, paragraph 62; page 5, paragraphs 69, 71-72 and 77-78; Table 1. Similarly, Table 2 demonstrates initial charging/discharging efficiencies of 74.5% and 74.1% in a gel electrolyte cell containing propylene carbonate when a graphite material obtained by sintering meso-carbon micro-beads is used as the anode material, whereas a significantly lower efficiency of only 56% is achieved in the same gel electrolyte cell when the anode material is substituted with a graphite material obtained by firing petroleum coke. See, Specification, page 5, paragraph 82; page 6, paragraphs 87-88 and 91-93; Table 2.

Appellants further submit that it would not have been obvious to combine the mesophase graphite particles of *Ozaki* with the propylene carbonate-containing cell of *MacFadden* because there would be no reasonable expectation of success in using a solvent containing propylene carbonate with the graphite particles of *Ozaki*. A reasonable expectation of success is required in order to properly combine references for an obviousness rejection. See, M.P.E.P. §2134.02 (2009). *Ozaki* expressly teaches that propylene carbonate is not suitable for use with its graphite particles because such a combination generates unfavorable side reactions. See, *Ozaki*, column 7, lines 5-16. Moreover, one of ordinary skill in the art would understand that the degree of decomposition of propylene carbonate depends on the physical properties of the graphite material, which vary based on the starting material and the production process of the graphite material. See, Specification, page 2, paragraph 21, lines 1-7. As such, one of ordinary skill in



the art would have had no reasonable expectation of success in merely substituting the mesophase graphite particles of *Ozaki* for the graphite particles in the propylene carbonate-containing cell of *MacFadden* to arrive at the present claims.

Moreover, one of ordinary skill in the art would have no reason to combine the graphite particles of *Ozaki* with the non-aqueous solid polymer electrolyte cell of *MacFadden* to arrive at the present claims because the references are directed to different problems in different fields of endeavor. The Examiner asserts that it would have been obvious to use the graphite particles of *Ozaki* with the solid polymer electrolyte cell of *MacFadden* merely because both references “teach nonaqueous secondary cells having a negative electrode including graphite and a nonaqueous electrolyte comprising a lithium salt and a mixed solvent.” See, Final Office Action, page 7, lines 3-5. However, “[t]he mere fact that references can be combined or modified does not render the resultant combination obvious unless the results would have been predictable to one of ordinary skill in the art.” See, M.P.E.P. §2143.01(III) (2009).

*Ozaki* is entirely directed to a non-aqueous liquid electrolyte cell including a negative electrode containing mesophase graphite particles. See, *Ozaki*, Abstract; column 2, lines 55-67; column 3, lines 1-14. *Ozaki* is completely unconcerned with the problems associated with gel electrolytes and instead teaches that its electrolyte is prepared “by dissolving LiPF<sub>6</sub> (1 mol/l) in a mixed solvent of ethylene carbonate, diethyl carbonate and methyl propionate in a 3:5:2 volume ratio” (thus resulting in a liquid electrolyte). See, *Ozaki*, column 4, lines 54-58. In contrast, *MacFadden* is directed to a solid polymer electrolyte cell having a lower impedance due to the intimate contact between the solid polymer electrolyte and the active electrode material when the solid polymer electrolyte is melted and impregnated into the electrodes. See, *MacFadden*, column 2, lines 66-67; column 3, lines 1-6 and 31-40. *MacFadden* is unconcerned with the properties of its anode active material and merely teaches that graphite or coke are suitable anode active materials. See, *MacFadden*, column 4, lines 9-15.

One of ordinary skill in the art would understand that the problems associated with non-aqueous liquid electrolyte cells are entirely distinguishable from those associated with non-aqueous gel electrolyte cells. For example, in a non-aqueous gel electrolyte cell, a graphite material having a smaller particle size is desirable to maintain a sufficient ion conductivity at the interface between the graphite particles and the gel electrolyte. See, Specification, page 2, paragraphs 22-23. If the particle size is too large, there is poor contact between the graphite

particles and the gel electrolyte, thereby increasing the impedance of the cell. See, Specification, page 2, paragraph 24, lines 1-7. However, this is not a problem in non-aqueous liquid electrolyte cells, where the liquid electrolyte can easily penetrate a space between the particles, thus scarcely producing an increased impedance despite a large size of the graphite particles. See, Specification, page 2, paragraph 24, lines 7-13. Therefore, in a non-aqueous liquid electrolyte cell using propylene carbonate in the electrolyte, it is desirable to use graphite having a large particle size because the contact area of the graphite material with the liquid electrolyte is smaller. See, Specification, page 2, paragraph 21, lines 7-15. As such, one of ordinary skill would have had no reason to substitute the graphite particles in the non-aqueous liquid electrolyte cell of *Ozaki* for the graphite particles in the non-aqueous gel electrolyte cell of *MacFadden* to arrive at the present claims with a reasonable expectation of success because the references are directed to different problems in different fields of endeavor.

Appellants respectfully submit that what the Examiner has done here is to apply hindsight reasoning by attempting to selectively piece together teachings of each of the references in an attempt to recreate what the claimed invention discloses. Appellants also submit that if it were proper for the Examiner to combine any references to arrive at the present claims simply because each reference suggests an element of the present claims, then every invention would effectively be rendered obvious. Instead, the skilled artisan must have a reason to combine the cited references to arrive at the present claims. Appellants respectfully submit that such a reason is not present in the instant case.

Accordingly, Appellants respectfully request that the rejection of Claims 26-32 and 35-39 under 35 U.S.C. §103(a) to *MacFadden* and *Ozaki* be reconsidered and withdrawn.

E. THE REJECTION OF CLAIMS 26-32 AND 35-39 UNDER 35 U.S.C. §103(a) TO AKASHI AND OZAKI SHOULD BE REVERSED BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS

For reasons similar to those set forth above, Appellants respectfully submit that the skilled artisan would have no reason to combine *Akashi* with *Ozaki* to arrive at the present claims because *Ozaki* teaches away from using its mesophase carbon particles with propylene carbonate. Similarly, it would not have been obvious to combine the mesophase carbon micro beads of *Ozaki* with the propylene carbonate solvent of *Akashi* to arrive at the present claims the

Specification demonstrates unexpected results when combining propylene carbonate with graphite obtained by firing meso-carbon micro beads. Moreover, it would not have been obvious to combine the mesophase graphite particles of *Ozaki* with the propylene carbonate-containing cell of *Akashi* to arrive at the present claims because there would be no reasonable expectation of success in using a solvent containing propylene carbonate with the graphite particles of *Ozaki*.

Appellants respectfully submit that what the Examiner has done here is to apply hindsight reasoning by attempting to selectively piece together teachings of each of the references in an attempt to recreate what the claimed invention discloses. Appellants also submit that if it were proper for the Examiner to combine any references to arrive at the present claims simply because each reference suggests an element of the present claims, then every invention would effectively be rendered obvious. Instead, the skilled artisan must have a reason to combine the cited references to arrive at the present claims. Appellants respectfully submit that such a reason is not present in the instant case.

Accordingly, Appellants respectfully request that the rejection of Claims 26-32 and 35-39 under 35 U.S.C. §103(a) to *Akashi* and *Ozaki* be reconsidered and withdrawn.

### VIII. CONCLUSION

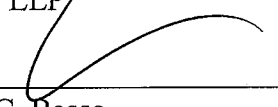
Appellants respectfully submit that the Examiner has failed to establish indefiniteness under 35 U.S.C. §112 and obviousness under 35 U.S.C. §103 with respect to the present claims. Accordingly, Appellants respectfully submit that the rejections are erroneous in law and in fact and should, therefore, be reversed by this Board.

The Director is authorized to charge \$540 for the Appeal Brief and any additional fees which may be required, or to credit any overpayment to Deposit Account No. 02-1818. If such a withdrawal is made, please indicate the Attorney Docket No. 3712174-00037 on the account statement.

Respectfully submitted,

K&L GATES LLP

BY

  
\_\_\_\_\_  
Thomas C. Basso  
Reg. No. 46,541  
Customer No. 29157

Dated: December 6, 2010

## CLAIMS APPENDIX

### PENDING CLAIMS ON APPEAL OF U.S. PATENT APPLICATION SERIAL NO. 09/162,992

26. A gel electrolyte secondary cell comprising:  
a positive electrode;  
a negative electrode comprising a current collector and a powder mixture composed of a graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ ; and  
a gel electrolyte comprising an electrolyte salt, a non-aqueous solvent and a high-molecular weight material,  
wherein the non-aqueous solvent comprises propylene carbonate and ethylene carbonate,  
wherein a content of propylene carbonate ranges from 10 mol% to 75 mol%,  
and wherein the graphite material is obtained by sintering meso-carbon micro-beads.
27. The gel electrolyte secondary cell according to claim 26 wherein the high-molecular weight material contains a nitrile group in a side chain thereof.
28. The gel electrolyte secondary cell according to claim 27 wherein the high-molecular weight material is polyacrylonitrile.
29. The gel electrolyte secondary cell according to claim 28 wherein a molar ratio of an acrylonitrile monomer to the non-aqueous solvent is 5:95 to 30:70.
30. The gel electrolyte secondary cell according to claim 26, wherein the electrolyte salt of the non-aqueous solvent is  $\text{LiPF}_6$  and wherein a concentration of  $\text{LiPF}_6$  with respect to non-aqueous solvent is 0.4 mol/cm<sup>3</sup> to 2 mol/cm<sup>3</sup>.
31. The gel electrolyte secondary cell according to claim 26 wherein the positive electrode contains a lithium-containing compound.
32. The gel electrolyte secondary cell according to claim 31 wherein the lithium-containing compound is a complex compound of lithium and a transition metal.

35. The gel electrolyte secondary cell according to claim 26 wherein the non-aqueous solvent includes at least one compound selected from the group consisting of  $\gamma$ -butyrolactone, methyl ethyl carbonate and dimethyl carbonate in addition to propylene carbonate and ethylene carbonate.

36. The gel electrolyte secondary cell according to claim 26 wherein the high molecular weight material has a number average molecular weight ranging from 5000 to 500000.

37. The gel electrolyte secondary cell according to claim 26 wherein the content of propylene carbonate is between 35 mol% and 75 mol %.

38. The gel electrolyte secondary cell according to claim 26 wherein the powder mixture of the negative electrode comprises a polyvinylidene fluoride binder.

39. The gel electrolyte secondary cell according to claim 26 wherein the graphite material is obtained by directly firing the meso-carbon micro-beads at a temperature between 2500° C and 3500° C.

**EVIDENCE APPENDIX**

EXHIBIT A: Non-final Office Action dated January 15, 2010

EXHIBIT B: Final Office Action dated July 2, 2010

EXHIBIT C: Notice of Panel Decision from Pre-Appeal Brief Review dated October 20, 2010

EXHIBIT D: U.S. Patent No. 5,772,934 to MacFadden ("*MacFadden*")

EXHIBIT E: U.S. Patent No. 6,280,878 B1 to Maruyama et al. ("*Maruyama*")

EXHIBIT F: U.S. Patent No. 5,522,127 to Ozaki et al. ("*Ozaki*")

EXHIBIT G: European Patent No. 0724305 B1 to Akashi ("*Akashi*")

**RELATED PROCEEDINGS APPENDIX**

None.



# EXHIBIT A



# UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE  
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/162,992	09/30/1998	TADASHI SENOO	P98-1703	9466
29175 K&L Gates LLP P. O. BOX 1135 CHICAGO, IL 60690	7590 01/15/2010		EXAMINER DOVE, TRACY MAE	
			ART UNIT 1795	PAPER NUMBER
			NOTIFICATION DATE 01/15/2010	DELIVERY MODE ELECTRONIC

**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

chicago.patents@klgates.com

<b>Office Action Summary</b>	<b>Application No.</b> 09/162,992	<b>Applicant(s)</b> SENOO ET AL.	
	<b>Examiner</b> TRACY DOVE	<b>Art Unit</b> 1795	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

### Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

### Status

- 1) ☒ Responsive to communication(s) filed on 10 November 2009.
- 2a) ☐ This action is **FINAL**.                      2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

### Disposition of Claims

- 4) ☒ Claim(s) 26-32 and 34-39 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 26-32 and 34-39 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

### Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.  
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).  
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

### Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All    b) ☐ Some \*    c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- \* See the attached detailed Office action for a list of the certified copies not received.

### Attachment(s)

- |  |   |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892)                                | 4) <input type="checkbox"/> Interview Summary (PTO-413)<br>Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)                       | 5) <input type="checkbox"/> Notice of Informal Patent Application                       |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08)<br>Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____  |

### **DETAILED ACTION**

This Office Action is in response to the communication filed on 11/10/09. Applicant's arguments have been considered, but are not persuasive. Claims 26-32 and 34-39 are pending. This Action is Non-FINAL.

#### ***Continued Examination Under 37 CFR 1.114***

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 11/10/09 has been entered.

#### ***Claims Analysis***

Claim 26 recites "classified by particle size adjustment to have a mean particle size of 5 to 100  $\mu\text{m}$ ", which appears to be a product-by-process limitation. The process that results in the claimed particle size is not given patentable weight. The claim will be examined as if it recited "graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ ".

Note "obtained by sintering mesocarbon micro-beads" in claim 34 and "is not ground" in claim 39 are product-by-process limitations that are not given patentable weight, in the absence of unexpected results.

#### ***Claim Rejections - 35 USC § 112***

The following is a quotation of the first paragraph of 35 U.S.C. 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the

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art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claim 39 is rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. The claim recites "wherein the graphite material is not ground", which does not appear to be supported by the specification as filed. Claim 26 recites "classified by particle size adjustment to have a mean particle size of 5 to 100  $\mu\text{m}$ ". It is unclear how the particle size is "adjusted" if the graphite material is not subjected to some type of grinding process. Examiner notes negative limitations must find proper support in the specification.

The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 26-32 and 34-39 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Claim 26 recites "classified by particle size adjustment", which is indefinite. It is unclear how the particles are "classified" and/or "adjusted".

### ***Claim Rejections - 35 USC § 103***

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

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(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 26-32 and 34-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over MacFadden, US 5,772,934 in view of Maruyama et al., US 6,280,878.

MacFadden teaches a lithium polymer battery comprising composite electrolyte-electrode sheets formed on current collectors that are then coated with solid polymer electrolyte (separate solid polymer electrolyte layer) prior to battery assembly (abstract). The SPE is located both internally and at the surface of the electrode structure (3:31-40). One or both of the electrodes of the battery can be further coated with additional SPE to provide an electrical insulator between electrodes of opposite polarity (5:27-40). The battery includes a cathode including a lithium transition metal compound (3:66-4:8), an anode including a carbon material such as graphite (4:9-15) and a solid polymer electrolyte (SPE) including a salt, a polymer and liquid. The electrolyte may include polyacrylonitrile (PAN) as the polymer,  $\text{LiPF}_6$  as the salt and a mixture of ethylene carbonate and propylene carbonate in a ratio of 70:30 to 30:70 as the liquid (5:11-20). The anode and the cathode include a current collector (3:45-48). The polymer is in an amount of 10-20 wt%, the liquid is in an amount of 65-75 wt% and the salt is in an amount of 5-12 wt% based on the SPE total weight (5:21-25). Example 2 has a specific teaching of 14 wt%  $\text{LiPF}_6$  salt, 11 wt% PAN and 75 wt% of ethylene carbonate/propylene carbonate. Other liquids suitable for use as the solvent include

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dimethyl carbonate, diethyl carbonate and  $\gamma$ -butyrolactone (2:21-28). The polymer binder may comprise polyvinylidene fluoride (clm 6).

MacFadden is silent regarding the mean particle size of the graphite material.

However, Maruyama teaches a lithium secondary gel electrolyte battery (title; abstract). The battery includes an electrode comprising a carbon active material. The carbon active material is preferably graphite having a mean particle size of 1 to 30  $\mu\text{m}$ , especially 5 to 25  $\mu\text{m}$ . Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because a smaller mean particle size tends to reduce the charge/discharge cycle life and to increase the variation of capacity. A larger mean particle size would lead to a significantly greater variation of capacity and a lower average capacity. It is believed that a variation of capacity results from a larger mean particle size because the contact of graphite with the collector and the contact between graphite particles become inconsistent (5:9-20). Thus, one of skill would have been motivated to provide the graphite particles of MacFadden with the mean particle size disclosed by Maruyama.

While MacFadden does not explicitly state the number average molecular weight of the PAN, this limitation is considered obvious in view of the teaching by MacFadden that PAN may be used as the polymer of the SPE. Regarding claim 30, Maruyama teaches the concentration of the electrolyte salt (such as  $\text{LiPF}_6$ ) in the electrolytic solution is preferably about 0.1 to 5 mol/liter and that maximum conductivity is generally available at a concentration of about 1 mol/liter (5:34-50). See also Example 1 of

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Maruyama. Claim 34 is a product-by-process limitation that is not given patentable weight.

\*

Claims 26-32 and 34-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over MacFadden, US 5,772,934 in view of Ozaki et al., US 5,522,127.

MacFadden teaches a lithium polymer battery comprising composite electrolyte-electrode sheets formed on current collectors that are then coated with solid polymer electrolyte (separate solid polymer electrolyte layer) prior to battery assembly (abstract). The SPE is located both internally and at the surface of the electrode structure (3:31-40). One or both of the electrodes of the battery can be further coated with additional SPE to provide an electrical insulator between electrodes of opposite polarity (5:27-40). The battery includes a cathode including a lithium transition metal compound (3:66-4:8), an anode including a carbon material such as graphite (4:9-15) and a solid polymer electrolyte (SPE) including a salt, a polymer and liquid. The electrolyte may include polyacrylonitrile (PAN) as the polymer,  $\text{LiPF}_6$  as the salt and a mixture of ethylene carbonate and propylene carbonate in a ratio of 70:30 to 30:70 as the liquid (5:11-20). The anode and the cathode include a current collector (3:45-48). The polymer is in an amount of 10-20 wt%, the liquid is in an amount of 65-75 wt% and the salt is in an amount of 5-12 wt% based on the SPE total weight (5:21-25). Example 2 has a specific teaching of 14 wt%  $\text{LiPF}_6$  salt, 11 wt% PAN and 75 wt% of ethylene carbonate/propylene carbonate. Other liquids suitable for use as the solvent include



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dimethyl carbonate, diethyl carbonate and  $\gamma$ -butyrolactone (2:21-28). The polymer binder may comprise polyvinylidene fluoride (clm 6).

MacFadden does not explicitly teach the graphite material has a mean particle size of 5 to 100  $\mu\text{m}$ . MacFadden does not explicitly teach the graphite material is obtained from meso-carbon micro beads.

However, Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). A favorable range of the specific surface area of the mesophase graphite particles is 1.0 to 8.0  $\text{m}^2/\text{g}$ , preferably 2.5 to 5.0  $\text{m}^2/\text{g}$  (6:50-58). The negative electrode was fabricated by mixing the mesophase graphite particles with styrene butadiene rubber (binder) to obtain a paste. A copper foil (current collector) of 0.02 mm thickness was coated with the paste of both surfaces. The concentration of  $\text{LiPF}_6$  with respect to the non-aqueous solvent is 1 mol/l ( $\text{mol}/\text{cm}^3$ ) (4:55-58).

Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because one of skill would have found it obvious to use the negative electrode of Ozaki for the negative electrode of MacFadden. Ozaki teaches that the negative electrode including mesophase graphite leads to smooth intercalating of lithium at charging over a wide temperature

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range resulting in an increased cell capacity (3:12-14). MacFadden teaches the negative electrode may be a carbonaceous material, preferably graphite, capable of intercalating lithium. Both Ozaki and MacFadden teach nonaqueous secondary cells having a negative electrode including graphite and a nonaqueous electrolyte comprising a lithium salt and a mixed solvent (4:54-58 of Ozaki). One of skill would have been motivated to use the graphite negative electrode of Ozaki as the graphite negative electrode of MacFadden because both materials are capable of intercalating lithium and the graphite negative electrode of Ozaki leads to increased cell capacity.

While MacFadden does not explicitly state the number average molecular weight of the PAN, this limitation is considered obvious in view of the teaching by MacFadden that PAN may be used as the polymer of the SPE.

\*

Claims 26-32 and 34-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over Akashi, EP 0724305 in view of Ozaki et al., US 5,522,127.

Akashi teaches a gel electrolyte and a lithium secondary cell using the gel electrolyte. The cell includes a positive electrode which may be a lithium/transition metal composite oxide, a negative electrode which may be a carbonaceous material such as graphite and the gel electrolyte (5:8:16). The non-aqueous solvent and the electrolyte salt used for the production of the gel electrolyte may be those generally used for the production of a lithium secondary cell. The solvent may preferably be ethylene carbonate (EC), propylene carbonate (PC),  $\gamma$ -butyl lactone or mixtures thereof. The preferred salt is  $\text{LiPF}_6$ . A mixture containing EC and PC in combination is preferred

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(4:1-12). The gel electrolyte further includes a polymer having a side chain to which at least one nitrile group is bonded. The polymer is preferably polyacrylonitrile (PAN) and has a number-average molecular weight ranging from about 50,000 to 500,000 (3:45-59). A molar ratio of a monomer as a repeating unit of the PAN to the non-aqueous solvent is suitably in the range of 5:95 to 30:70 though it varies depending upon kinds of the non-aqueous solvent, the gelling agent and the electrolyte salt used. The lithium salt may be in a concentration of 0.4 to 2 M (4:13-17; 31-32). Tables 1 & 2 teach a gel electrolyte including PAN, EC and PC where PC is 10-38 mol% of the gel electrolyte.

Akashi does not specifically teach the negative electrode of claim 26. Akashi teaches lithium secondary cells are well known to have a negative electrode made of a material such as lithium, a lithium alloy or a carbonaceous material capable of occluding lithium (2:12-17). Akashi further teaches examples of suitable negative electrode activating ingredients may include lithium, a lithium alloy and a carbonaceous material capable of occluding lithium, such as graphite (5:12-16).

However, Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). A favorable range of the specific surface area of the mesophase graphite particles is 1.0 to 8.0  $\text{m}^2/\text{g}$ , preferably 2.5 to 5.0  $\text{m}^2/\text{g}$  (5:50-58). The negative

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electrode was fabricated by mixing the mesophase graphite particles with styrene butadiene rubber (binder) to obtain a paste. A copper foil (current collector) of 0.02 mm thickness was coated with the paste of both surfaces.

Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because one of skill would have found it obvious to use the negative electrode of Ozaki for the negative electrode of Akashi. Ozaki teaches that the negative electrode including mesophase graphite leads to smooth intercalating of lithium at charging over a wide temperature range resulting in an increased cell capacity (3:12-14). Akashi teaches the negative electrode may be a carbonaceous material such as graphite that is capable of occluding lithium (intercalating). Both Ozaki and Akashi teach nonaqueous secondary cells having a negative electrode including graphite and a nonaqueous electrolyte comprising a lithium salt and a mixed solvent (4:54-58 of Ozaki). One of skill would have been motivated to use the graphite negative electrode of Ozaki as the graphite negative electrode of Akashi because both materials are capable of intercalating lithium and the graphite negative electrode of Ozaki leads to increased cell capacity.

Akashi teaches polyvinylidene fluoride is a known electrode binder (page 10, lines 33-34).

### ***Response to Arguments***

Applicant's arguments filed 11/10/09 have been fully considered but they are not persuasive. Applicant argues neither MacFadden nor Ozaki disclose or suggest a graphite material classified by particle size adjustment to have a mean particle size of 5

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to 100  $\mu\text{m}$  (e.g., a material that is not ground). However, "classified by particle size adjustment to have a mean particle size of 5 to 100  $\mu\text{m}$ " is a product-by-process limitation. The process that results in the claimed particle size is not given patentable weight. The claim was examined as if it recited "graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ ". Ozaki teaches the average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). Furthermore, at least claim 26 does not recite a graphite material that is not ground. Note any evidence of unexpected results must distinguish the claimed invention over the prior art of record. Claim 39 contains a product-by-process limitation and is rejected for containing new matter.

Applicant again argues Ozaki suggests that propylene carbonate is disfavored. This argument has been addressed by the Board of Patent Appeals (and the Examiner) and has been determined to be non-persuasive.

Applicant argues neither Akashi nor Ozaki disclose or suggest a graphite material classified by particle size adjustment to have a mean particle size of 5 to 100  $\mu\text{m}$  (e.g., a material that is not ground). However, "classified by particle size adjustment to have a mean particle size of 5 to 100  $\mu\text{m}$ " is a product-by-process limitation. The process that results in the claimed particle size is not given patentable weight. The claim was examined as if it recited "graphite material having a mean particle size of 5 to 100  $\mu\text{m}$ ". Ozaki teaches the average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). Furthermore, at least claim 26 does not recite a graphite material that is not ground. Note any evidence of unexpected results

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must distinguish the claimed invention over the prior art of record. Claim 39 contains a product-by-process limitation and is rejected for containing new matter. Akashi teaches the claimed percentage of propylene carbonate in the electrolyte solvent and Ozaki teaches the claimed negative electrode material.

Applicant again argues Ozaki suggests that propylene carbonate is disfavored. This argument has been addressed by the Board of Patent Appeals (and the Examiner) and has been determined to be non-persuasive. Applicant has not addressed the Examiner's motivation for combining MacFadden and Ozaki or Akashi and Ozaki nor has Applicant shown the claimed negative electrode material has unexpected properties over the negative electrode material disclosed by Ozaki. In response to applicant's arguments against the references individually, one cannot show nonobviousness by attacking references individually where the rejections are based on combinations of references. See *In re Keller*, 642 F.2d 413, 208 USPQ 871 (CCPA 1981); *In re Merck & Co.*, 800 F.2d 1091, 231 USPQ 375 (Fed. Cir. 1986).

Examiner points out that the section of Ozaki cited by Applicant as assertedly teaching away from the claimed invention (col. 2, lines 3-6) is part of the background section of Ozaki. Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The

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average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). Thus, Applicant's arguments are not persuasive.

***Conclusion***

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Tracy Dove whose telephone number is 571-272-1285. The examiner can normally be reached on Monday & Tuesday (9:00-5:30).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Pat Ryan can be reached on 571-272-1292. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

January 11, 2010

/TRACY DOVE/

Primary Examiner, Art Unit 1795

<b>Notice of References Cited</b>	Application/Control No. 09/162,992	Applicant(s)/Patent Under Reexamination SENOO ET AL.	
	Examiner TRACY DOVE	Art Unit 1795	Page 1 of 1

**U.S. PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,280,878	08-2001	Maruyama et al.	429/233
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

**FOREIGN PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

**NON-PATENT DOCUMENTS**

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

\*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)  
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.



**To:** chicago.patents@klgates.com,,  
**From:** PAIR\_eOfficeAction@uspto.gov  
**Cc:** PAIR\_eOfficeAction@uspto.gov  
**Subject:** Private PAIR Correspondence Notification for Customer Number 29175

Jan 15, 2010 08:34:10 PM

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Application	Document	Mailroom Date	Attorney Docket No.
09162992	CTNF	01/15/2010	P98-1703
	CTNF	01/15/2010	P98-1703
	892	01/15/2010	P98-1703

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# EXHIBIT B



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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/162,992	09/30/1998	TADASHI SENOO	3712174.00037	9466
29175	7590	07/02/2010		
K&L Gates LLP P. O. BOX 1135 CHICAGO, IL 60690			EXAMINER DOVE, TRACY MAE	
			ART UNIT 1795	PAPER NUMBER
			NOTIFICATION DATE 07/02/2010	DELIVERY MODE ELECTRONIC

**Please find below and/or attached an Office communication concerning this application or proceeding.**

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<b>Office Action Summary</b>	Application No. 09/162,992	Applicant(s) SENOO ET AL.	
	Examiner TRACY DOVE	Art Unit 1795	

**-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --**

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 15 April 2010.
- 2a) ☒ This action is **FINAL**.                      2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 26-32 and 35-39 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 26-32 and 35-39 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.  
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).  
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).  
a) ☐ All    b) ☐ Some \*    c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
  2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
  3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- \* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- |  |   |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892)   | 4) <input type="checkbox"/> Interview Summary (PTO-413)<br>Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)                       | 5) <input type="checkbox"/> Notice of Informal Patent Application                       |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08)<br>Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____  |

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### **DETAILED ACTION**

This Office Action is in response to the communication filed on 4/15/10.

Applicant's arguments have been considered, but are not persuasive. Claims 26-32 and 35-39 are pending. This Action is FINAL.

#### ***Claims Analysis***

Note "obtained by sintering meso-carbon micro-beads" in claim 26 and "obtained by directly firing the meso-carbon micro-beads at a temperature between 2500°C and 3500°C" in claim 39 are product-by-process limitations that are not given patentable weight, in the absence of unexpected results.

#### ***Claim Rejections - 35 USC § 112***

The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claim 39 is rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Claim 26 recites "obtained by sintering" and claim 39 recites "obtained by directly firing", which appear to be reciting the same step. It is improper to use different terms to refer to the same element of the claims (improper antecedent basis). Examiner suggests claim 26 be amended to recite "obtained by firing" and claim 39 recite "according to claim 26, wherein said firing is at a temperature between 2500°C and 3500°C". Alternatively, Examiner suggests claim 39 be amended to recite "according to claim 26, wherein said sintering is at a temperature between 2500°C and 3500°C".

***Claim Rejections - 35 USC § 103***

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 26-32 and 35-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over MacFadden, US 5,772,934 in view of Maruyama et al., US 6,280,878.

MacFadden teaches a lithium polymer battery comprising composite electrolyte-electrode sheets formed on current collectors that are then coated with solid polymer electrolyte (separate solid polymer electrolyte layer) prior to battery assembly (abstract). The SPE is located both internally and at the surface of the electrode structure (3:31-40). One or both of the electrodes of the battery can be further coated with additional SPE to provide an electrical insulator between electrodes of opposite polarity (5:27-40). The battery includes a cathode including a lithium transition metal compound (3:66-4:8), an anode including a carbon material such as graphite (4:9-15) and a solid polymer electrolyte (SPE) including a salt, a polymer and liquid. The electrolyte may include polyacrylonitrile (PAN) as the polymer,  $\text{LiPF}_6$  as the salt and a mixture of ethylene carbonate and propylene carbonate in a ratio of 70:30 to 30:70 as the liquid (5:11-20). The anode and the cathode include a current collector (3:45-48). The polymer is in an amount of 10-20 wt%, the liquid is in an amount of 65-75 wt% and the salt is in an amount of 5-12 wt% based on the SPE total weight (5:21-25). Example 2 has a specific

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teaching of 14 wt%  $\text{LiPF}_6$  salt, 11 wt% PAN and 75 wt% of ethylene carbonate/propylene carbonate. Other liquids suitable for use as the solvent include dimethyl carbonate, diethyl carbonate and  $\gamma$ -butyrolactone (2:21-28). The polymer binder may comprise polyvinylidene fluoride (clm 6).

MacFadden is silent regarding the mean particle size of the graphite material.

However, Maruyama teaches a lithium secondary gel electrolyte battery (title; abstract). The battery includes an electrode comprising a carbon active material. The carbon active material is preferably graphite having a mean particle size of 1 to 30  $\mu\text{m}$ , especially 5 to 25  $\mu\text{m}$ . Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because a smaller mean particle size tends to reduce the charge/discharge cycle life and to increase the variation of capacity. A larger mean particle size would lead to a significantly greater variation of capacity and a lower average capacity. It is believed that a variation of capacity results from a larger mean particle size because the contact of graphite with the collector and the contact between graphite particles become inconsistent (5:9-20). Thus, one of skill would have been motivated to provide the graphite particles of MacFadden with the mean particle size disclosed by Maruyama.

While MacFadden does not explicitly state the number average molecular weight of the PAN, this limitation is considered obvious in view of the teaching by MacFadden that PAN may be used as the polymer of the SPE. Regarding claim 30, Maruyama teaches the concentration of the electrolyte salt (such as  $\text{LiPF}_6$ ) in the electrolytic solution is preferably about 0.1 to 5 mol/liter and that maximum conductivity is generally

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available at a concentration of about 1 mol/liter (5:34-50). See also Example 1 of Maruyama. The limitation "obtained by sintering meso-carbon micro-beads" is a product-by-process limitation that is not given patentable weight.

\*

Claims 26-32 and 35-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over MacFadden, US 5,772,934 in view of Ozaki et al., US 5,522,127.

MacFadden teaches a lithium polymer battery comprising composite electrolyte-electrode sheets formed on current collectors that are then coated with solid polymer electrolyte (separate solid polymer electrolyte layer) prior to battery assembly (abstract). The SPE is located both internally and at the surface of the electrode structure (3:31-40). One or both of the electrodes of the battery can be further coated with additional SPE to provide an electrical insulator between electrodes of opposite polarity (5:27-40). The battery includes a cathode including a lithium transition metal compound (3:66-4:8), an anode including a carbon material such as graphite (4:9-15) and a solid polymer electrolyte (SPE) including a salt, a polymer and liquid. The electrolyte may include polyacrylonitrile (PAN) as the polymer,  $\text{LiPF}_6$  as the salt and a mixture of ethylene carbonate and propylene carbonate in a ratio of 70:30 to 30:70 as the liquid (5:11-20). The anode and the cathode include a current collector (3:45-48). The polymer is in an amount of 10-20 wt%, the liquid is in an amount of 65-75 wt% and the salt is in an amount of 5-12 wt% based on the SPE total weight (5:21-25). Example 2 has a specific teaching of 14 wt%  $\text{LiPF}_6$  salt, 11 wt% PAN and 75 wt% of ethylene carbonate/propylene carbonate. Other liquids suitable for use as the solvent include



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dimethyl carbonate, diethyl carbonate and  $\gamma$ -butyrolactone (2:21-28). The polymer binder may comprise polyvinylidene fluoride (clm 6).

MacFadden does not explicitly teach the graphite material has a mean particle size of 5 to 100  $\mu\text{m}$ . MacFadden does not explicitly teach the graphite material is obtained from meso-carbon micro beads.

However, Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). A favorable range of the specific surface area of the mesophase graphite particles is 1.0 to 8.0  $\text{m}^2/\text{g}$ , preferably 2.5 to 5.0  $\text{m}^2/\text{g}$  (6:50-58). The negative electrode was fabricated by mixing the mesophase graphite particles with styrene butadiene rubber (binder) to obtain a paste. A copper foil (current collector) of 0.02 mm thickness was coated with the paste of both surfaces. The concentration of  $\text{LiPF}_6$  with respect to the non-aqueous solvent is 1 mol/l ( $\text{mol}/\text{cm}^3$ ) (4:55-58).

Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because one of skill would have found it obvious to use the negative electrode of Ozaki for the negative electrode of MacFadden. Ozaki teaches that the negative electrode including mesophase graphite leads to smooth intercalating of lithium at charging over a wide temperature

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range resulting in an increased cell capacity (3:12-14). MacFadden teaches the negative electrode may be a carbonaceous material, preferably graphite, capable of intercalating lithium. Both Ozaki and MacFadden teach nonaqueous secondary cells having a negative electrode including graphite and a nonaqueous electrolyte comprising a lithium salt and a mixed solvent (4:54-58 of Ozaki). One of skill would have been motivated to use the graphite negative electrode of Ozaki as the graphite negative electrode of MacFadden because both materials are capable of intercalating lithium and the graphite negative electrode of Ozaki leads to increased cell capacity.

While MacFadden does not explicitly state the number average molecular weight of the PAN, this limitation is considered obvious in view of the teaching by MacFadden that PAN may be used as the polymer of the SPE.

\*

Claims 26-32 and 35-39 are rejected under 35 U.S.C. 103(a) as being unpatentable over Akashi, EP 0724305 in view of Ozaki et al., US 5,522,127.

Akashi teaches a gel electrolyte and a lithium secondary cell using the gel electrolyte. The cell includes a positive electrode which may be a lithium/transition metal composite oxide, a negative electrode which may be a carbonaceous material such as graphite and the gel electrolyte (5:8:16). The non-aqueous solvent and the electrolyte salt used for the production of the gel electrolyte may be those generally used for the production of a lithium secondary cell. The solvent may preferably be ethylene carbonate (EC), propylene carbonate (PC),  $\gamma$ -butyl lactone or mixtures thereof. The preferred salt is  $\text{LiPF}_6$ . A mixture containing EC and PC in combination is preferred

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(4:1-12). The gel electrolyte further includes a polymer having a side chain to which at least one nitrile group is bonded. The polymer is preferably polyacrylonitrile (PAN) and has a number-average molecular weight ranging from about 50,000 to 500,000 (3:45-59). A molar ratio of a monomer as a repeating unit of the PAN to the non-aqueous solvent is suitably in the range of 5:95 to 30:70 though it varies depending upon kinds of the non-aqueous solvent, the gelling agent and the electrolyte salt used. The lithium salt may be in a concentration of 0.4 to 2 M (4:13-17; 31-32). Tables 1 & 2 teach a gel electrolyte including PAN, EC and PC where PC is 10-38 mol% of the gel electrolyte.

Akashi does not specifically teach the negative electrode of claim 26. Akashi teaches lithium secondary cells are well known to have a negative electrode made of a material such as lithium, a lithium alloy or a carbonaceous material capable of occluding lithium (2:12-17). Akashi further teaches examples of suitable negative electrode activating ingredients may include lithium, a lithium alloy and a carbonaceous material capable of occluding lithium, such as graphite (5:12-16).

However, Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). A favorable range of the specific surface area of the mesophase graphite particles is 1.0 to 8.0  $\text{m}^2/\text{g}$ , preferably 2.5 to 5.0  $\text{m}^2/\text{g}$  (5:50-58). The negative

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electrode was fabricated by mixing the mesophase graphite particles with styrene butadiene rubber (binder) to obtain a paste. A copper foil (current collector) of 0.02 mm thickness was coated with the paste of both surfaces.

Therefore, the invention as a whole would have been obvious to one having ordinary skill in the art at the time the invention was made because one of skill would have found it obvious to use the negative electrode of Ozaki for the negative electrode of Akashi. Ozaki teaches that the negative electrode including mesophase graphite leads to smooth intercalating of lithium at charging over a wide temperature range resulting in an increased cell capacity (3:12-14). Akashi teaches the negative electrode may be a carbonaceous material such as graphite that is capable of occluding lithium (intercalating). Both Ozaki and Akashi teach nonaqueous secondary cells having a negative electrode including graphite and a nonaqueous electrolyte comprising a lithium salt and a mixed solvent (4:54-58 of Ozaki). One of skill would have been motivated to use the graphite negative electrode of Ozaki as the graphite negative electrode of Akashi because both materials are capable of intercalating lithium and the graphite negative electrode of Ozaki leads to increased cell capacity.

Akashi teaches polyvinylidene fluoride is a known electrode binder (page 10, lines 33-34).

### ***Response to Arguments***

Applicant's arguments filed 4/15/10 have been fully considered but they are not persuasive. Applicant argues neither MacFadden nor Maruyama disclose or suggest a graphite material having a mean particle size of 5 to 100  $\mu\text{m}$  wherein the graphite

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material is obtained by sintering meso-carbon micro-beads. However, Maruyama teaches the carbon active material is preferably graphite having a mean particle size of 1 to 30  $\mu\text{m}$ , especially 5 to 25  $\mu\text{m}$ . Furthermore, the process that results in the claimed particle size of the graphite material is not given patentable weight.

Applicant asserts unexpected results are shown in Tables 1 & 2 of the specification. However, Comparative Examples 1 & 2 are not representative of the prior art of record. Maruyama teaches a graphite material having a mean particle size of 5-100  $\mu\text{m}$ . Note any evidence of unexpected results must distinguish the claimed invention over the prior art of record. Furthermore, Examples 1-4 are not commensurate in scope with the claimed invention (no mean particle size disclosed).

Applicant again argues Ozaki suggests that propylene carbonate is disfavored. This argument has been addressed by the Board of Patent Appeals (and the Examiner) and has been determined to be non-persuasive. Applicant has not addressed the Examiner's motivation for combining MacFadden and Ozaki or Akashi and Ozaki nor has Applicant shown the claimed negative electrode material has unexpected properties over the negative electrode material disclosed by Ozaki. In response to applicant's arguments against the references individually, one cannot show nonobviousness by attacking references individually where the rejections are based on combinations of references. See *In re Keller*, 642 F.2d 413, 208 USPQ 871 (CCPA 1981); *In re Merck & Co.*, 800 F.2d 1091, 231 USPQ 375 (Fed. Cir. 1986).

Examiner points out that the section of Ozaki cited by Applicant as assertedly teaching away from the claimed invention (col. 2, lines 3-6) is part of the background

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section of Ozaki. Ozaki teaches a non-aqueous electrolyte secondary cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium is possible (1:8-12). The negative electrode is made from mesophase graphite particles. The mesophase graphite particles are produced from micro beads of mesophase carbon made from pitch (3:1-7). The average particle diameter of the graphite particles is in the range of 3-10  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  (6:35-43). Thus, Applicant's arguments are not persuasive.

### ***Conclusion***

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO MONTHS** of the mailing date of this final action and the advisory action is not mailed until after the end of the **THREE-MONTH** shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than **SIX MONTHS** from the date of this final action.

Art Unit: 1795

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Tracy Dove whose telephone number is 571-272-1285. The examiner can normally be reached on Monday & Tuesday (9:00-5:30).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Pat Ryan can be reached on 571-272-1292. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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June 28, 2010

/TRACY DOVE/

Primary Examiner, Art Unit 1795

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Application	Document	Mailroom Date	Attorney Docket No.
09162992	CTFR	07/02/2010	3712174.00037

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# EXHIBIT C



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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/162,992	09/30/1998	TADASHI SENOO	3712174.00037	9466
29175	7590	10/20/2010	EXAMINER	
K&L Gates LLP			DOVE, TRACY MAE	
P. O. BOX 1135			ART UNIT	PAPER NUMBER
CHICAGO, IL 60690			1726	
			MAIL DATE	DELIVERY MODE
			10/20/2010	PAPER

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<b>Notice of Panel Decision from Pre-Appeal Brief Review</b>	Application/Control No.	Applicant(s)/Patent under Reexamination	
	09/162,992	SENOO ET AL.	
	BENJAMIN UTECH	Art Unit	
		1797	

This is in response to the Pre-Appeal Brief Request for Review filed 4 October 2010.

1. ☐ **Improper Request** – The Request is improper and a conference will not be held for the following reason(s):

- ☐ The Notice of Appeal has not been filed concurrent with the Pre-Appeal Brief Request.
- ☐ The request does not include reasons why a review is appropriate.
- ☐ A proposed amendment is included with the Pre-Appeal Brief request.
- ☐ Other: .

The time period for filing a response continues to run from the receipt date of the Notice of Appeal or from the mail date of the last Office communication, if no Notice of Appeal has been received.

2. ☒ **Proceed to Board of Patent Appeals and Interferences** – A Pre-Appeal Brief conference has been held. The application remains under appeal because there is at least one actual issue for appeal. Applicant is required to submit an appeal brief in accordance with 37 CFR 41.37. The time period for filing an appeal brief will be reset to be one month from mailing this decision, or the balance of the two-month time period running from the receipt of the notice of appeal, whichever is greater. Further, the time period for filing of the appeal brief is extendible under 37 CFR 1.136 based upon the mail date of this decision or the receipt date of the notice of appeal, as applicable.

- ☒ The panel has determined the status of the claim(s) is as follows:
- Claim(s) allowed: \_\_\_\_\_.
- Claim(s) objected to: \_\_\_\_\_.
- Claim(s) rejected: 26-32 & 35-39.
- Claim(s) withdrawn from consideration: \_\_\_\_\_.

3. ☐ **Allowable application** – A conference has been held. The rejection is withdrawn and a Notice of Allowance will be mailed. Prosecution on the merits remains closed. No further action is required by applicant at this time.

4. ☐ **Reopen Prosecution** – A conference has been held. The rejection is withdrawn and a new Office action will be mailed. No further action is required by applicant at this time.

All participants:

(1) BENJAMIN UTECH.

(3) Tracy Dove./

(2) /Patrick Ryan/.

(4) \_\_\_\_\_.

/Benjamin L. Utech/  
Primary Examiner

# EXHIBIT D



US005772934A

# United States Patent [19]

## MacFadden

[11] Patent Number: **5,772,934**  
 [45] Date of Patent: **Jun. 30, 1998**

[54] **PROCESS TO PRODUCE LITHIUM-POLYMER BATTERIES**

[75] Inventor: **Kenneth Orville MacFadden**,  
Highland, Md.

[73] Assignee: **W. R. Grace & Co.-Conn.**, New York,  
N.Y.

[21] Appl. No.: **653,173**

[22] Filed: **May 24, 1996**

[51] Int. Cl.<sup>6</sup> ..... **H01M 6/18**

[52] U.S. Cl. .... **264/42; 264/45.9; 264/48;**  
264/344; 429/190; 429/192; 429/194

[58] Field of Search ..... 264/49, 48, 344,  
264/129, 42, 45.9; 429/128, 188, 192, 190,  
194

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Primary Examiner—Allan R. Kuhns

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### [57] ABSTRACT

A polymer bonded sheet product suitable for use as an electrode in a non-aqueous battery system. A porous electrode sheet is impregnated with a solid polymer electrolyte, so as to diffuse into the pores of the electrode. The composite is allowed to cool, and the electrolyte is entrapped in the porous electrode. The sheet products composed have the solid polymer electrolyte composition diffused into the active electrode material by melt-application of the solid polymer electrolyte composition into the porous electrode material sheet. The solid polymer electrolyte is maintained at a temperature that allows for rapid diffusion into the pores of the electrode. The composite electrolyte-electrode sheets are formed on current collectors and can be coated with solid polymer electrolyte prior to battery assembly. The interface between the solid polymer electrolyte composite electrodes and the solid polymer electrolyte coating has low resistance.

19 Claims, 1 Drawing Sheet

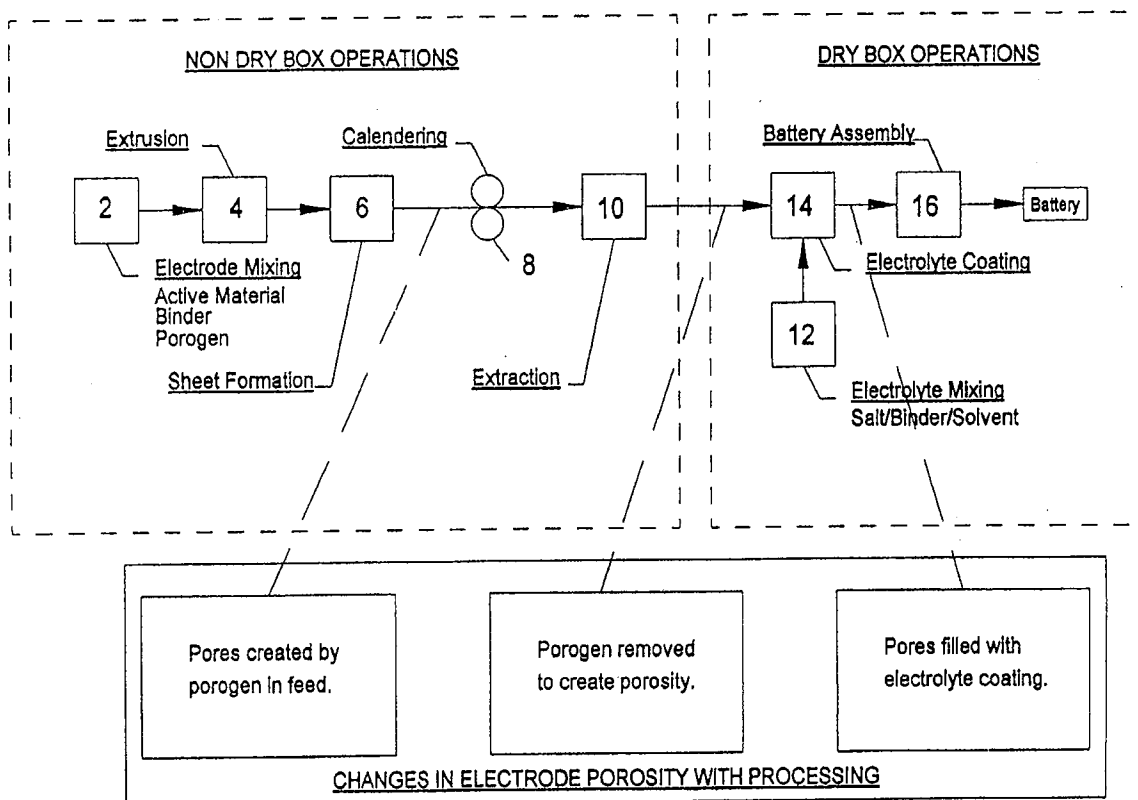
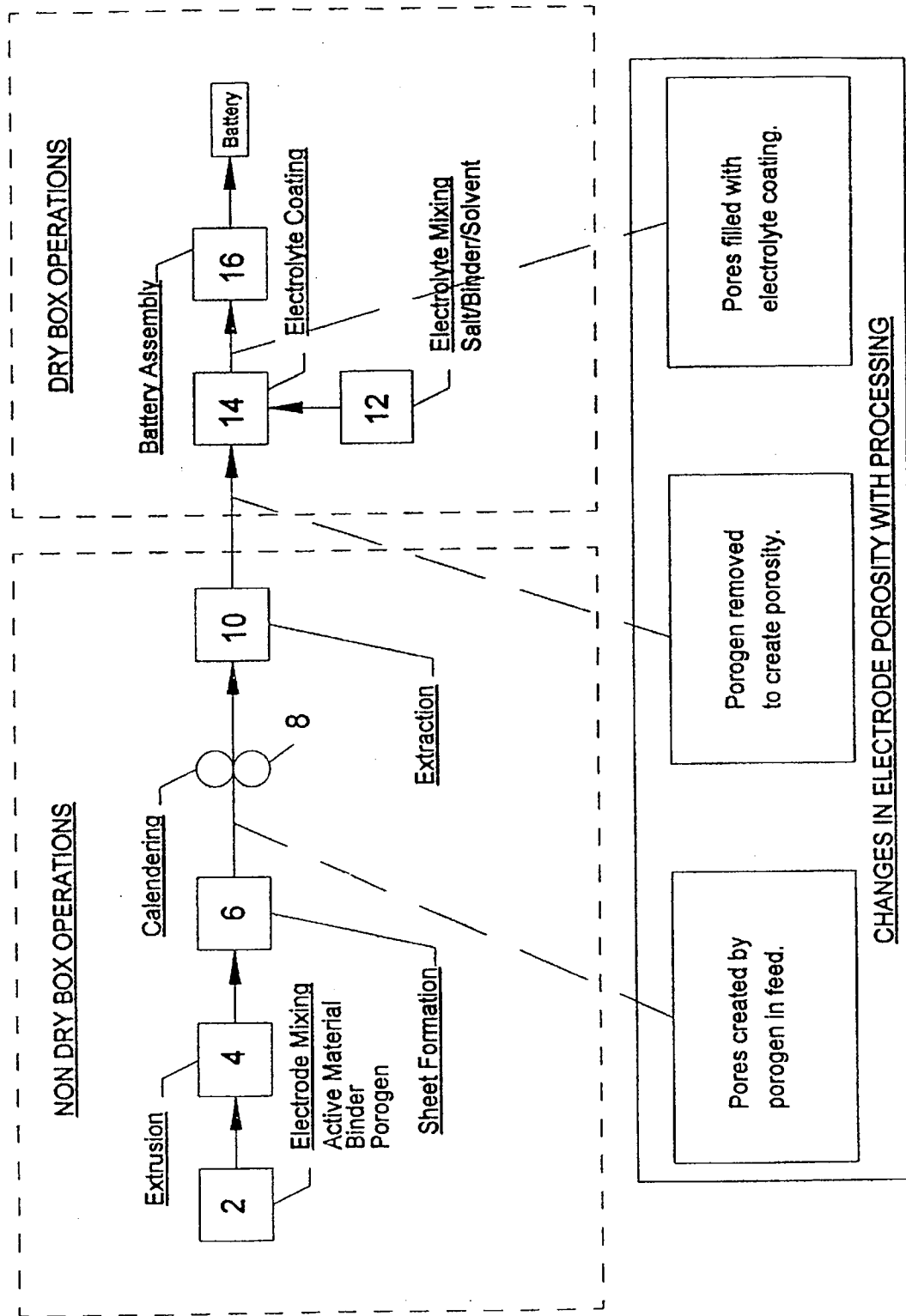


FIG. 1



## PROCESS TO PRODUCE LITHIUM-POLYMER BATTERIES

This invention was made with Government support under Contract DE-FC02-91CE50336 awarded by the United States Department of Energy. The Government has certain rights in this invention.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to solid polymer electrolyte-electrode composites useful in non-aqueous batteries, and to battery systems containing such composites. More specifically, the present invention relates to electrolyte-electrode composites fabricated by preparing a porous electrode and applying a fluidized solid polymer electrolyte to diffuse into the pores of the electrode. The composite is allowed to cool, and the electrolyte is entrapped in the porous electrode.

#### 2. Description of the Related Art

Storage batteries have a configuration composed of at least one pair of electrodes of opposite polarity, generally arranged in a series of adjacent electrodes of alternating polarity. The current flow between electrodes is maintained by an electrolyte composition capable of carrying ions between electrode pairs.

Non-aqueous batteries have certain distinct advantages over other types of storage batteries. They use light-weight metals, such as the alkali metals as, for example, lithium. The metals are preferably in forms that are capable of intercalating with the conductive material, such as carbon. Typical metals and metal compounds include alkali metals and alkali metal compounds, such as lithium metal, lithium oxides, lithium-aluminum alloys and the like, which are at the far end of the electromotive series. These batteries have the potential for providing much higher specific (gravimetric) energy and volumetric energy densities (capacity per unit weight and volume, respectively) than other types of batteries.

The improved potential, in part, is due to the low atomic weight of the metals utilized, and the high potential for forming a battery in conjunction with suitable positive electrodes far removed in the electromotive series from the light weight metal (alkali metal) electrode. The battery can be formed in any conventional physical design, such as cylindrical, rectangular or disc-shaped "button" cells, normally of a closed cell configuration.

The battery components include positive electrodes, negative electrodes, and an insulating material capable of permitting ionic conductivity such as porous separator sheet or a solid polymer electrolyte located between the electrodes. Batteries formed of these components can be in the form of alternating plates in a sandwich design, or of a continuously spirally-wound "jelly-roll" design, as are well known.

Both positive and negative electrodes have been formed by processing compositions composed of electrochemically active and electrolytically conductive materials with an inert polymer (e.g. polyolefins, polytetrafluoroethylenes and the like) capable of bonding the materials into the desired shaped electrode. For example, polymer bonded electrodes are conventionally formed by mixing the solid, active particulate components together with a high temperature stable polymer, such as poly(tetrafluoroethylene), processed into the desired shape by pressing and then subjected to heat to provide a sintered, fused porous product. Alternately, the

active materials are mixed with a thermoplastic polymer, such as a polyolefin together with an inert liquid, such as a hydrocarbon oil and then shaped into a sheet product, by pressing, extrusion or the like. The oil or other liquid is then removed by extraction to provide a resultant porous sheet product.

The polymer bonded electrodes are of a porous design which permit electrolyte liquid to enter into the internal porosity and permit ionic transfer to more readily occur with the electrode's internally positioned active material.

Electrolytes found useful in the present high energy battery systems can be in the form of a gel or solid polymer electrolyte (SPE) such as described in U.S. Pat. No. 5,219,679 to Abraham et al., the disclosure of which is incorporated herein by reference. Such SPE systems are composed, in general, of a polymer matrix in which ions are conducted and which contain lithium ion ( $\text{Li}^+$ ) exchange complexes. The complexes utilize lithium salts that are well known in the art of lithium battery production. The lithium salts commonly used include  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiClO}_4$ , for example.

Liquids that have been utilized effectively in making the ion-exchange complexes of the SPE include the organic solvents, and especially those that are aprotic, i.e., not prone to contributing a proton, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, dimethyl adipate, tetramethylene sulphone,  $\gamma$ -butyrolactone, dimethylformamide, dioctyl phthalate, dibutyl phthalate and the like.

Polymers typically used in SPE's include polyacrylonitrile (PAN), poly(tetraethylene glycol diacrylate) (PEGDA), poly(vinylidene difluoride) (PVDF) and poly(vinyl pyrrolidone) (PVP).

The known solid polymer electrolytes typically have been used to make batteries by sandwiching preformed sheet-like members of SPE's between a cathode and an anode, as shown, for example, in U.S. Pat. No. 4,818,643, issued to Cook et al., which is incorporated herein by reference. Therein, a solid polymer electrolyte is sandwiched between a composite cathode disc and a lithium metal anode. The composite cathode disc is pressed from a mixture of polyethylene oxide and active cathode material.

In forming the battery, additional solvent may be added to the system to permit electrolyte solvent introduction into the pore volume of the electrode members.

Disadvantageously, high impedances are formed at the interfaces between the various layers, which are essentially plane surfaces. Accordingly, efforts have been made in the prior art to enhance the adhesion properties of the various cell layers. This is done, for example, by providing surface asperities, typically greater than one micron.

The known processes are disadvantageous due to insufficient adhesion and high resistance/impedance at the interface between the electrodes and the electrolytes, which continues to be a problem in batteries resulting from the processes. In addition, the known processes are disadvantageous in that many steps must be completed under dry-atmosphere conditions.

Accordingly, the need exists for an improved lithium battery having reduced resistance at the interfaces between electrolytes and electrodes. In addition, the need exists for methods of producing battery electrodes for such batteries that require a reduced number of process steps, and a reduced number of process steps that must be carried out under dryatmosphere conditions.

### SUMMARY OF THE INVENTION

The present invention overcomes the deficiencies of the prior art, such as those noted above, by providing a com-

posite electrolyte-electrode that includes a solid polymer electrolyte diffused into a porous electrode material. The process generally involves formation of a porous electrode material, melting a solid polymer electrolyte composition, and applying the melted composition to at least one surface of the electrodes material to cause it to impregnate therein. The solid polymer electrolyte has been found to diffuse into the pores of the electrode material to form the composite electrolyte-electrodes. The present invention also includes electrodes formed by the process, and battery cells made with the composite electrolyte-electrodes.

Advantageously, the solid polymer electrolyte applied by the present process comes into more intimate contact with the active electrode material to form the composite electrolyte-electrodes. Both anodes and cathodes can be fabricated by the process. The anodes and cathodes thus formed can be assembled directly into batteries.

In addition the solid polymer electrolyte containing hygroscopic lithium salts can be added to the final step, thus minimizing the amount of processing performed in a dry atmosphere.

### BRIEF DESCRIPTION OF THE FIGURE

FIG. 1 is a block flow diagram of a production process according to a preferred embodiment of the present invention.

### DETAILED DESCRIPTION OF THE INVENTION

The present process provides a polymer-bonded electrode/SPE composite product which has been found to have improved impedance (lower impedance) due to the intimate contact between the SPE and the active electrode material located both internally and at the surface of the electrode structure. Further, the present process provides a means of fabricating battery components and resultant cell structures under ambient conditions for a portion of formation process, thus alleviating the conventional dry-atmosphere conditions during said portion.

Porous polymer-bonded electrodes are initially formed by conventional methods, such as those disclosed in U.S. Pat. Nos. 5,143,805; 4,791,037; 4,654,281; 4,735,875; and 4,731,310 to Anderman et al. which teachings are incorporated herein by reference. The electrodes generally comprise at least one microporous sheet and current collector composed of conductive material in intimate contact with each microporous sheet. The microporous sheet is a free-standing sheet composed of 70-98 wt. % electrochemically active and electrically conductive particles and 2-30 wt. % polyethylene. The electrochemically active particles comprise a metal chalcogenide having a metal selected from Ti, Zr, Hf, Nb, Cu, Fe, Ta, V, Mn, Cr, Co, Ni and mixtures of these metals alone or together with intercalated metals, such as lithium or sodium and up to 30 wt. % conductive particles, such as carbon of particle size 1-100 nm. The polyethylene has molecular weight of about 150,000 to 5,000,000. The electrode may contain up to 5 wt. % organic plasticizer.

The porous electrodes contemplated herein can be formed by various methods known in the prior art. Typically, the electrodes are formed by mixing electrochemically active material with electrically conductive electrode materials, a binder and a porogen. The porogen is removed subsequently to create porosity.

Porous cathodic electrodes according to the invention preferably utilize a metal chalcogenide as the electrochemi-

cally active material. Preferred chalcogenides are alkali metal (e.g. lithium) salts of manganese oxides, cobalt oxides, vanadium oxides, nickel oxides or mixed oxides and mixtures thereof. The most preferred are lithium manganese dioxide ( $\text{LiMn}_2\text{O}_4$ ) or overlithiated manganese oxides. The preferred conductive material may be a carbon black, such as acetylene black, which is mixed with the active material in the cathode.

The active electrode material suitable for producing anodes of the present invention are preferably carbons capable of having lithium intercalated within the crystal or other structure of the carbon material. The preferred forms of carbon include graphite and coke. The carbon preferably is finely ground. The active electrode materials preferably are in the form of a dry particulate.

The binder used in forming the electrode is a thermoplastic polymeric material having a melting point preferably above about 150° C. The specific polymer will depend on the desired electrode design. The preferred polymers are high temperature melting point thermoplastic polymers, such as polyolefins as, for example homopolymers of polyethylene, polypropylene and the like and copolymers thereof which have been formed with other ethylenically polymerizable monomers, such as butadiene, pentadiene, acrylates, acrylonitrile and the like.

A porogen, such as a hydrocarbon oil, is included in the electrode mix. The porogen is subsequently removed to form the pores in the electrode.

The electrode is formed by conventional means in which the electrically conductive material, electrochemically active material, binder and the porogen are mixed and shaped into a sheet product by pressing, extrusion or the like. The sheet product may be further processed to draw it down or subject it to calender rolls to provide the desired thickness (normally 2 to 50 mils) and then the porogen is removed such as by contacting the sheet product with a material which a solvent for the porogen and a nonsolvent for the remaining components. These operations are normally conducted under ambient conditions to provide a porous electrode structure.

In accordance with the present invention, the formed porous electrode sheet product is contacted with a solid polymer electrolyte gel composition which is heated sufficiently to provide a fluid, low viscosity material. The exact temperature of the SPE at application will depend upon its specific composition and resultant physical characteristics. The application temperature should be high enough to provide a low viscosity, fluid material at a temperature which is lower than the degradation temperature of the components forming both the SPE and the electrode to which it is to be applied. Further, it must be lower than the deformation temperature of the recipient electrode. Typical temperatures range from about 80° C. to about 140° C. with from about 100° C. to 140° C. being preferred.

The SPE materials useful in the present invention are high viscosity substantially solid (capable of retaining its form) materials at ambient and normal operating conditions of the battery and are capable of being low viscosity, fluid materials at elevated, nondegradation temperatures. The SPE is separately formed, heated to a temperature to cause the SPE to be fluid and applied to at least one surface of the previously formed, porous electrode sheet material to cause it to impregnate into and substantially fill the electrode's pore volume. Whether the SPE is applied to one or to both major surfaces of the electrode will depend on the electrode's design. If a current collector is internally located in



the interior of the electrode, the SPE may be applied on one or both surfaces. If the current collector is located on one surface of the electrode, the SPE will be applied to the opposite major surface.

The SPE can be applied by any conventional means. Preferably the SPE fluid is applied directly to the electrode surface and doctored with a knife blade. The SPE is thus caused to enter and occupy the pore volume of the electrode. The SPE can be applied in a single or, optionally, a multi-application process.

The solid polymer electrolyte (SPE) which are useful in the present process includes a salt, a binder, and liquid. Polymers such as polyethylene oxide, polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF) or the like, including suitable copolymer systems, may be used. Of the known lithium salts, such as those noted above,  $\text{LiPF}_6$  is most preferred. Of the liquids noted above, preferably ethylene carbonate, propylene carbonate, or a mixture of the two, in ratio of 70:30 to 30:70 and most preferably 50:50 would be utilized.

The solid polymer electrolyte components are present in the following amounts: polymer in from about 10 to 20 weight percent; liquid in from about 65 to 75 weight percent and salt in from about 5 to 12 weight percent based on the SPE total weight.

Once the composite electrolyte-electrode has been formed, it is ready to be assembled with an electrode of opposite polarity into a battery cell. Optionally, one or both of the electrodes can be further coated with additional solid polymer electrolyte composition to provide an electrical insulator between electrodes of opposite polarity. The solid polymer electrolyte composition is similar to that described above used to melt-coat the porous electrode. Because the solid polymer electrolyte used in the initial application to enter the pore volume of the electrode is the same or similar to that applied as the electrical insulator/electrolyte coating on at least one major surface of the resultant composite product, the impedance normally associated with interface incompatibility is substantially alleviated.

Other features and advantages of the present invention will become apparent from the following description of the invention, which refers to the drawing.

Referring to FIG. 1, a porous electrode material, including an active electrode material, a binder, and a porogen, are initially mixed 2, and then extruded 4. Electrode sheets are formed at stage 6. Pores are created in the sheet by the porogen in the feed. The porous electrode can be formed in various ways known in the art. For example, a pore former such as a hydrocarbon oil, can be included in the electrode mix.

The composition optionally can also include additives, such as dispersants, colorants and the like to improve processing and the characteristics of the final product.

Subsequently, the sheet is calendared at stage 8, and subjected to an extraction process 10. As a result of the extraction, the porogen is removed, leaving pores in the electrode sheet. During extrusion, the pore former can be removed using a solvent, for example. Advantageously, steps 2 through 10 can be performed in an ambient atmosphere, i.e., without using a dry-atmosphere environment. Prior to extraction, the electrode can be coated onto a current collector, which can be a mesh material to allow extraction to take place through the current collector.

The remainder of the process preferably is done in a dry-atmosphere environment. Prior to being introduced into this environment, the electrode may be subjected to heat

(e.g. an air oven) to remove any trace water. A solid polymer electrolyte is mixed at stage 12. The solid polymer electrolyte includes a salt, a binder and a solvent. The solid polymer electrolyte composition is applied at stage 14 in a manner to cause it to impregnate the pore volume of the porous electrode.

The solid polymer electrolyte diffuses into the pores of the porous electrode to form the composite electrolyte-electrode. In order to enhance the diffusion, the solid polymer electrolyte preferably is applied while the electrode is still warm. Most preferably, the melt-coating is performed at a temperature (e.g.  $130^\circ\text{C}$ .) where the viscosity of the solid polymer electrolyte composition is low enough to permit rapid diffusion into the pores of the electrode. The solid polymer electrolyte can be applied either by a single application or by multiple applications, in sufficient amount to both fill the pore volume of the electrode and provide a coating thereon. The porous electrode and the diffused solid polymer electrolyte then cool to form the final composite electrolyte-electrode product.

The present invention provides composite electrolyte-electrodes fabricated according to the processes above. The composite electrolyte-electrodes can be either a cathode or an anode. The composite electrolyte-electrodes can then be formed into batteries 16.

This invention provides for electrode products having enhanced interfacial relationship between the SPE and electrode and provide a battery exhibiting lower impedance than those formed from electrode and SPE sheet materials, as conventionally known.

The following specific examples are provided by way of illustration, and are not meant to be a limitation on the invention as defined by the claims appended hereto. All parts and percentages are by weight unless otherwise indicated.

#### EXAMPLE 1

A polyethylene-based electrode is produced by extruding polyethylene mixed with a pore former such as a hydrocarbon oil and a solid which acts as the active material (graphite for the anode and  $\text{Mn}_2\text{O}_4$  or other metal oxide for the cathode, for example). The electrode is comprised of the materials outlined plus a current collector which is either co-extruded with the active material in a cross-head die or laminated to the electrode material after extraction. When using a coextrusion current collector, the collector is a mesh material to allow extraction.

After extrusion of the electrode material, the pre-formed electrode (oil, polyethylene and solid) is extracted with a solvent, such as hexane or a chlorinated hydrocarbon, for example, to remove the pore forming oil, which is recycled. The porous electrode can be stored at ambient conditions prior to further use.

The porous electrode and current collector is fed into a glove box containing a dry atmosphere where it is heated to remove residual water. The electrode is then melt coated with a solid polymer electrolyte composition of the following formulation: The SPE is coated onto the electrode at  $130^\circ\text{C}$  where the viscosity is low enough to permit rapid diffusion into the pores of the electrode. The resultant product contains electrolyte within the pores of the electrode to provide an electrolyte-electrode composite product.

#### EXAMPLE 2

A layer of solid polymer electrolyte for coating onto a composite electrolyte-electrode of Example 1 has the following formulation:

Component	weight %
LiPF <sub>6</sub> salt	14
Polyacrylonitrile	11
Ethylene carbonate/ propylene carbonate	75

The electrolyte-cathode film from Example 1 is coated with a film of the extruded solid polymer electrolyte above to form a laminate of solid polymer electrolyte and composite electrolyte-electrode that is ready for assembly into cells, to form a battery, for example. Preferably, the solid polymer electrolyte and the extruded composite electrolyte-electrode layer are still warm when they are brought together.

Advantageously, substantial intermixing takes place at the interface of the cathode composition and the solid polymer electrolyte when the two similarly-composed extrusion layers are brought into contact while still warm. Accordingly, the surfaces of the two layers blend together to form an "interfaceless" laminate that is ready for assembly into cells. As a further advantage, the solid polymer electrolyte layer acts as a separator for the cathode.

Although the present invention has been described in relation to particular embodiments thereof, many other variations and modifications and other uses will become apparent to those skilled in the art. The present invention is to be limited not by the specific disclosure herein, but only by the appended claims.

What is claimed is:

1. A process for forming a solid polymer electrolyte-electrode composite comprising the steps of:

forming an electrode comprising active material, binder and porogen;

removing at least a portion of the porogen to provide a porous electrode;

applying to the porous electrode a fluid, low viscosity mixture of components of a solid polymer electrolyte composition comprising electrolyte salt, polymer binder and electrolyte liquid, said application being conducted at an elevated temperature sufficient to cause said composition to be a fluid, low viscosity mixture, and said binder of the solid polymer electrolyte has a lower melt (deformation onset) thermal properties than the binder of the electrode;

diffusing the applied electrolyte mixture into the pores of the electrode to form a composite product; and

cooling the composite product, the solid polymer electrolyte being entrapped in the porous electrode.

2. The process of claim 1, wherein the porous electrode comprises active material composed of at least one electrically conductive and at least one electrochemically active material.

3. The process of claim 2, wherein the binder of the electrode is a thermoplastic polymer having a melting point above about 150° C.

4. The process of claim 1, wherein the electrode binder component comprises at least one polyolefin.

5. The process of claim 1, wherein the electrolyte salt is at least one lithium salt.

6. The process of claim 1, wherein the polymer binder of the solid polymer electrolyte comprises the polyethylene oxide, polyacrylonitrile or polyvinylidene difluoride or mixtures thereof.

7. The process of claim 1, further comprising extruding the electrode onto a metallic current collector.

8. The process of claim 1 wherein the active material of said electrode comprises carbon.

9. The process of claim 1 wherein the active material of said electrode comprises a light-weight metal or a light-weight metal chalcogenide.

10. The process of claim 9, wherein the metal is an alkali metal.

11. The process of claim 1, further comprising the step of removing residual water.

12. The process of claim 1, wherein the step of applying is performed at a temperature at which the viscosity of the solid polymer electrolyte is low enough to permit rapid diffusion into the pores of the electrode.

13. The process of claim 1, further comprising the step of over-coating the cooled composite product with a polymeric separator.

14. The process of claim 13, wherein the polymer separator is electronically non-conductive at all temperatures.

15. The process of claim 14, wherein the polymer separator composition includes a salt, a solvent, and a polymer selected from the group consisting of polyethylene oxide, polyacrylonitrile, and polyvinylidene fluoride.

16. The process of claim 13, wherein both the solid polymer electrolyte and the polymeric separator include the same polymer, solvent, and lithium salt.

17. The process of claim 15, wherein the solid polymer electrolyte comprises polyacrylonitrile.

18. The process of claim 2, wherein the solid active electrode material is in the form of a particulate.

19. The process of claim 8, wherein the active electrode material is carbon capable of intercalating lithium ions.

\* \* \* \* \*

# EXHIBIT E



US006280878B1

(12) **United States Patent**  
**Maruyama et al.**

(10) **Patent No.:** **US 6,280,878 B1**  
(45) **Date of Patent:** **\*Aug. 28, 2001**

(54) **ELECTRODE AND LITHIUM SECONDARY BATTERY USING THIS ELECTRODE**

(75) **Inventors:** **Satoshi Maruyama**, Chiba; **Masato Kurihara**, Tokyo; **Akira Kakinuma**, Akita, all of (JP)

(73) **Assignee:** **TDK Corporation**, Tokyo (JP)

(\*) **Notice:** This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** **09/086,581**

(22) **Filed:** **May 29, 1998**

(30) **Foreign Application Priority Data**

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(51) **Int. Cl.<sup>7</sup>** ..... **H01M 4/64**

(52) **U.S. Cl.** ..... **429/233; 429/236; 429/245; 429/231.1; 429/231.8; 429/330; 429/300; 429/304**

(58) **Field of Search** ..... **429/304, 300, 429/129, 233, 236, 245, 330, 231.1, 231.8**

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3,985,574	10/1976	Feuillade et al. ....	429/162
4,470,859 *	9/1984	Benezra et al. ....	429/254
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5,434,024 *	7/1995	Ikeda et al. ....	429/234
5,436,091 *	7/1995	Shackie et al. ....	429/192
5,470,357	11/1995	Schmutz et al. ....	429/192
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5,858,264 *	1/1999	Ichino et al. ....	429/192

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*Primary Examiner*—Laura Weiner

(74) *Attorney, Agent, or Firm*—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

(57) **ABSTRACT**

An electrode comprising a porous metal member in sheet form having a three-dimensional skeleton structure and a solid polymer electrolyte is used to construct a lithium secondary battery and an electric double-layer capacitor. Owing to the increased retaining force of the gel electrolyte component to a current collector, the gel electrolyte component can be directly applied to the current collector, contributing to mass scale productivity and cost reduction.

**16 Claims, No Drawings**

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# ELECTRODE AND LITHIUM SECONDARY BATTERY USING THIS ELECTRODE

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to an electrode structure having a current collector of a lithium secondary battery, electric double-layer capacitor or the like, and a lithium secondary battery and electric double-layer capacitor using the electrode.

### 2. Background Art

Secondary batteries for use in notebook size personal computers, video cameras and the like are required to have a high energy density and a satisfactory charge/discharge cycle life. The secondary batteries which have been used heretofore include lead acid batteries, nickel-cadmium batteries, and nickel-hydrogen batteries. Lithium secondary batteries were proposed and have been used in practice as a secondary battery having a higher energy density.

In the prior art, liquids are used as the electrolyte of such secondary batteries. If the electrolyte is made solid, it is attractive as batteries of the next generation type because solid electrolytes can prevent liquid leakage and enables sheet structuring. In particular, if lithium ion secondary batteries which now enjoy rapid widespread use in notebook size personal computers and the like can be structured into a sheet form or multilayer compact size, they are expected to find a wider range of application.

In order that such solid electrolytes be used, it is proposed to construct them as ceramic materials, polymeric materials or composite materials. Among others, gel electrolytes which are plasticized using a polymeric electrolyte and an electrolytic solution are considered promising in the development of electrolytes because they have both the high conductivity of liquids and the plasticity of polymers.

An example of utilizing a gel electrolyte in a battery is already disclosed in U.S. Pat. No. 3,985,574. This patent includes examples in which a polyacetal which has been gelled by incorporating therein a supporting electrolyte such as ammonium perchlorate and a solvent such as propylene carbonate is used as a separator or positive electrode. A battery is constructed using lithium as the negative electrode. The positive electrode is prepared by bonding a honeycomb grid to a metal such as silver under heat and pressure and applying the gel thereto. Further, U.S. Pat. No. 5,296,318 discloses a practical system.

Specifically, U.S. Pat. No. 5,296,318 discloses that a copolymer of poly(vinylidene fluoride) with hexafluoropropylene is used as polymeric matrices of a positive electrode, negative electrode and separator of a lithium intercalation battery. The key feature of this disclosure is the use of the specific copolymer. The reason why characteristics can be improved is believed to be that since not only a binder alone is added to the electrode, but a gel electrolyte composition is also mixed during formation of the electrode, the electrode well matches with the electrolyte so that the internal resistance can be reduced. That is, unlike the solution system, an electrode composition inherent to the gel electrolyte system (referred to as gel electrode composition, hereinafter) is constructed.

Further, U.S. Pat. No. 5,470,357 discloses an electrode structure wherein a metal grid of aluminum or copper is used as the current collector. The method of making electrodes involves forming a film of a gel electrode composition and then bonding a metal grid thereto by the application of heat

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and pressure. The electrode composition cannot be applied to the grid during formation of the electrode because when a practical slurry is used, it cannot be fully held by the grid. Also, the results of our study showed that the use of a copolymer of poly(vinylidene fluoride) with hexafluoropropylene as the gel electrolyte was impractical because adhesion between the electrode and the collector metal was weak. Accordingly, it is believed that the manufacturing process described in Examples of U.S. Pat. No. 5,470,357 is used in practice. More particularly, it is necessary to previously coat the collector with a paint in which a conductive aid is mixed with a polymeric matrix component in a gel electrolyte, a paste in which a conductive material is added to a hot-melt paint as shown in the above-referred patent, or a conductive paint for use in electrolytic capacitors. Usually, the electrode (film+collector) is prepared by bonding the thus obtained grid to the gel electrode composition film under heat and pressure. It is thus apparent that a special step is necessary during formation of the electrode, leading to a reduced mass productivity and an increased cost.

## SUMMARY OF THE INVENTION

An object of the invention is to provide an electrode capable of increasing the retaining force of a gel electrolyte component to a collector for enabling direct coating of the gel electrolyte component to the collector and thus featuring improved mass productivity and a reduced cost; and to provide a lithium secondary battery and an electric double-layer capacitor using the electrode.

The above object is achieved by the following construction.

- (1) An electrode comprising a porous metal member in sheet form having a three-dimensional skeleton structure and a solid polymer electrolyte.
- (2) The electrode of (1) wherein said solid polymer electrolyte comprises a gelled polymer matrix containing an electrolytic solution.
- (3) The electrode of (1) wherein said porous metal member has a porosity of 80 to 98% and a mean maximum pore diameter of 100 to 800  $\mu\text{m}$ .
- (4) A lithium secondary battery comprising the electrode of (1).
- (5) An electric double-layer capacitor comprising the electrode of (1).

## FUNCTION

With the above-described problems borne in mind, we made investigations on the electrode which is easier to manufacture. We have found that the desired electrode can be obtained by tailoring the electrode structure using a porous metal member having a three-dimensional skeleton structure. That is, a porous metal member having a three-dimensional skeleton structure is used as the collector instead of the grid, thereby increasing the retaining force of a gel electrolyte component to the collector for enabling direct coating or printing of the gel electrolyte component to the collector. Further, as will be described later, since the porous metal member having a three-dimensional skeleton structure is contained within the electrode, the internal resistance of the electrode is reduced and rated properties are improved. This advantage is attributable to the porous metal member having a three-dimensional skeleton structure as used herein, and becomes more prominent when a gel electrolyte favored by the invention is used.

It is already disclosed in JP-A 315768/1992 to apply to the collector a porous metal member having a three-dimensional

skeleton structure. In this patent, the porous metal member is used in a nickel-oxygen battery for the purpose of preventing the active material from separating from the collector surface. As opposed to this, in the present invention, the porous metal member having a three-dimensional skeleton structure plays not only the role of holding the active material, but also the role of holding the gelled electrolyte.

When the gelled solid polymer electrolyte favored by the invention is used, mere contact of the active material with the collector surface is not important, but the co-presence of three phases which are the collector, the gelled solid polymer electrolyte and the active material is important. Herein, the active material must be in contact with the collector, with a conductive aid interposed therebetween. In the case of a solution system, a three-phase coexisting region is generally formed even when the active material is not in contact with the collector because the solution fully penetrates internally. Therefore, a three-phase interface is formed even when it is not positively intended to form such an interface, and direct coating to a foil is possible. However, in the even where the solid electrolyte is used, if the active material is in direct contact with the collector surface, the formation of a three-phase interface becomes difficult and electrode reaction is extremely obstructed. Therefore, the collector/conductive aid/solid polymer electrolyte joint is necessary as described above, for which the porous metal member having a three-dimensional skeleton structure must be used.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now the illustrative construction of the present invention is described in detail.

The electrode of the invention comprises a porous metal member in sheet form having a three-dimensional skeleton structure and a solid polymer electrolyte. By combining the porous metal member having a three-dimensional skeleton structure with the solid polymer electrolyte, there can coexist the three phases of a collector, a gelled solid polymer electrolyte and an active material. It then becomes possible to directly coat the gelled solid polymer electrolyte to the collector, and hence, to produce an electrode of high performance at a high efficiency.

##### Porous Metal Member

To prepare the porous metal member having a three-dimensional skeleton structure used herein, a spongy plastic foam having a three-dimensional reticulated skeleton structure or synthetic fiber sheet is coated with a metal or alloy by such methods as plating and thermal spraying, obtaining a porous metal. Examples of the metal to be applied include copper, nickel, aluminum, iron, chromium, zinc, tin, lead, silver, cadmium, cobalt, gold, and platinum. When the electrode is applied to lithium secondary batteries, copper, nickel, stainless steel or the like is preferred for the negative electrode, and aluminum or the like is preferred for the positive electrode. Examples of the spongy plastic foam having a three-dimensional reticulated skeleton structure or synthetic fiber sheet to be coated include foams of plastics such as polyesters, styrene, vinyl chloride, polyacrylonitrile, polyisocyanate, polypropylene and polyethylene, and synthetic fibers of polyethylene, polypropylene, polyesters, polyvinyl alcohol, polyurethane, polyamides, regenerated cellulose, etc. Preferred are foams of polyurethane (urethane foams).

After the metal or alloy is applied to the spongy plastic foam or synthetic fiber sheet, the foam or sheet is heated and roasted whereby the foam or sheet is removed. This is followed by annealing treatment, leaving a porous metal member having a three-dimensional skeleton structure.

The porous or cellular metal member preferably has a porosity of about 80 to 98%, especially about 90 to 95%, and a mean maximum pore diameter of about 100 to 800  $\mu\text{m}$ , especially about 250 to 500  $\mu\text{m}$ , as calculated from equivalent circles to surface-exposed pores. The porosity and mean pore diameter can be determined by observing the surface under a scanning electron microscope (SEM). The porous metal member is of sheet form, preferably having a thickness of about 0.1 to 3 mm, more preferably about 0.3 to 1 mm, and especially about 0.4 to 0.6 mm.

##### Polymer for Solid Electrolyte

The polymer used herein for the solid electrolyte is not critical. The intended use in electrochemical application requires that the polymer be stable against voltage and have satisfactory thermal and mechanical properties. For this reason, well-known gel type SPE polymers are preferable. Exemplary polymers include chemically crosslinked gels obtained by polymerizing an acrylate containing ethylene oxide which is a photo-polymerizable monomer with a polyfunctional acrylate, polyacrylonitrile, polyethylene oxide, and polypropylene oxide; and physically crosslinked gels based on fluorinated polymers such as polyvinylidene fluoride (PVDF), vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-chlorotrifluoroethylene copolymers P(VDF-CTFE), vinylidene fluoride-hexafluoropropylene fluoro-rubber, vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene fluoro-rubber, and vinylidene fluoride-tetrafluoroethylene-perfluoroalkyl vinyl ether fluoro-rubber. The preferred vinylidene fluoride base polymers contain at least 50% by weight, especially at least 70% by weight of vinylidene fluoride (VDF). Of the above-mentioned polymers, polyvinylidene fluoride, abbreviated as PVDF, copolymers of vinylidene fluoride (VDF) with hexafluoropropylene (HFP), and copolymers of vinylidene fluoride (VDF) with chlorotrifluoroethylene (CTFE), abbreviated as P(VDF-CTFE), are preferred.

These polymers are commercially available. For example, VDF-CTFE copolymers are commercially available under the trade name of Sefral Soft G150 and G180 from Central Glass K.K. and Soref 31508 from Nippon Solvay K. K. VDF-HFP copolymers are commercially available under the trade name of KynarFlex 2750 (VDF:HFP=85:15 wt %) and KynarFlex 2801 (VDF:HFP=90:10 wt %) from Elf Atochem and Soref 11008, Solef 11010, Solef 21508 and Solef 21510 from Nippon Solvay K.K.

##### Solvent of Electrolytic Solution

As the solvent of the electrolytic solution, those solvents which do not undergo decomposition under a high voltage applied are preferred when the intended application to lithium secondary batteries and capacitors is taken into account. Exemplary solvents used herein are non-aqueous solvents and include carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, dimethyl carbonate (DMC), diethyl carbonate, and ethyl methyl carbonate; and tetrahydrofuran (THF), 2-methyltetrahydrofuran, 1,3-dioxolan, 4-methyldioxolan,  $\gamma$ -butyrolactone, sulfolane, 3-methylsulfolane, dimethoxyethane, diethoxyethane, ethoxymethoxyethane, and ethyl diglyme. Although the quantitative ratio of the solvent to the polymer depends on the type of the solvent and the polymer used, it is preferred to add about 40 to 100% by weight of the polymer to the solvent. Also although the quantitative ratio of the polymer-mixed solvent to the electrolyte depends on the type of the polymer-mixed solvent and the electrolyte used, it is preferred to add about 0.5 to 2 mol/liter of the electrolyte to the polymer-mixed solvent.

### Active Material

When the electrode of the invention is used in lithium secondary batteries, it is preferred to use such an active material as carbon, lithium metal, lithium alloy or oxide materials as the negative electrode active material and to use such an active material as oxide or carbon capable of intercalating and deintercalating lithium ions as the positive electrode active material.

The carbon used as the active material may be properly selected from natural or artificial graphite, resin fired carbon materials, and carbon fibers. They are used in powder form. Preferred among these is graphite desirably having a mean particle size of 1 to 30  $\mu\text{m}$ , especially 5 to 25  $\mu\text{m}$ . A smaller mean particle size tends to reduce the charge/discharge cycle life and to increase the variation of capacity (between individual cells). A larger mean particle size would lead to a significantly greater variation of capacity and a lower average capacity. It is believed that a variation of capacity results from a larger mean particle size because the contact of graphite with the collector and the contact between graphite particles become inconsistent.

Composite oxides containing lithium are preferred as the oxide capable of intercalating and deintercalating lithium ions. Such oxides are, for example,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiV}_2\text{O}_4$ .

Also, where the electrode of the invention is used in electric double-layer capacitors, it is preferred to use the above-described activated carbon as the active material.

The active material is preferably added to a mixed solution of the polymer and the electrolyte in a ratio of the active material to the mixed solution of from about 97/3 to about 40/60 although the ratio varies with the type of the active material.

### Electrolyte

The electrolyte is preferably selected from electrolyte salts in dissolved form such as  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiSO}_3\text{CF}_3$ , and  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$  when the application to lithium batteries is taken into account. Also, quaternary ammonium salts such as tetraethylammonium perchlorate and tetraethylammonium fluoroborate are useful as well as the foregoing alkali metal salts containing lithium when the electrolyte is used in electric double-layer capacitors. An appropriate electrolyte salt compatible with the solvent may be selected from these and other examples depending on the electro-chemical device to which the invention is applied. These electrolyte salts may be used alone, or a plurality of salts may be used in a predetermined mix ratio. The concentration of the electrolyte salt in the electrolytic solution of non-aqueous solvent system is preferably about 0.1 to 5 mol/liter. Maximum conductivity is generally available at a concentration of about 1 mol/liter.

### Method

Now it is described how to prepare the electrode of the invention.

First, there is furnished a spongy plastic foam having a three-dimensional reticulated skeleton structure or synthetic fiber sheet as the skeleton member. In the case of a urethane foam, for example, a sheet-shaped urethane foam is used as the skeleton member, and is given conductivity, for example, by immersing in a solution having graphite dispersed, followed by drying and solidification, or by electroless plating.

The foam is further provided with a layer of a metal or alloy such as copper, nickel, stainless steel or aluminum by such techniques as electrolytic plating, electroless plating and thermal spraying. At this point, the metal or alloy preferably builds up to a thickness of about 50 to 100  $\mu\text{m}$ .

The skeleton member having the metal or alloy layer coated thereon is heat treated for removing the skeleton

member. Preferably the heating temperature is equal to or above the temperature at which the skeleton member burns or gasifies, but below the melting point of the metal or alloy layer and especially about 450 to 600° C. If desired, the porous metal member from which the skeleton member has been removed is subject to heat treatment for annealing purpose. The annealing temperature is preferably about 600 to 1,200° C. although it varies with the type of the metal or alloy layer. The porous metal member is then cut to the predetermined shape, obtaining a collector.

Next, a coating solution is prepared by dispersing the electrode material such as carbon material in a polymer solution. The solvent used for the coating solution may be selected as appropriate from various solvents in which the polymer is soluble. For example, *N,N*-dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone, acetone, methyl ethyl ketone, and methyl isobutyl ketone may be used.

The dispersing/dissolving step may be carried out by adding filler particles to the polymer solution, and mixing the mixture for dispersion and dissolution at room temperature or elevated temperature using a mixer such as a magnetic stirrer or homogenizer or a dispersing apparatus such as a ball mill, super sand mill or pressure kneader.

The concentration and viscosity of the coating solution may be determined as appropriate depending on the coating means. Usually, the concentration of the polymer in the solvent is preferably 3 to 30% by weight. The amount of the polymer added is preferably about 3 to 20 parts by weight per 100 parts by weight of the electrode material. For example, where the electrode material is a carbon material, the ratio of the carbon material to the polymer is preferably in the range from 85/15 to 94/6% by weight. A less amount of the polymer would lead to insufficient adhesion whereas an excessive amount of the polymer would lead to a reduced battery capacity or capacitor capacitance.

The means for applying the coating solution to the collector is not critical and may be determined as appropriate depending on the material and shape of the collector. In general, doctor blade coating, electrostatic painting, dipping, spraying, roll coating, metal mask printing, gravure coating and screen printing techniques are used. Thereafter, rolling treatment is carried out by means of a platen press or calender roll, if necessary.

The coating solution is coated to the collector and dried, forming a coating. The coating solution is preferably applied to such an extent that all the pores in the collector are filled with the coating solution and the entire surface of the collector (excluding connections to lead terminals) is covered with the coating solution.

Where the electrode of the invention is used as the electrode of a lithium secondary battery, the electrolytic solution is prepared by dissolving a lithium-containing electrolyte in a non-aqueous solvent. The lithium-containing electrolyte may be selected from  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiAsF}_6$ , for example. The non-aqueous solvent may be selected from ethers, ketones, carbonates, and organic solvents as exemplified in JP-A 121260/1988, for example.

The use of the above-described polymer binder leads to a substantially improved charge/discharge cycle life. If the above-described polymer is not used as the binder for the active material, the battery capacity would gradually decrease upon repetitive charge/discharge cycles because the polymer can be gradually dissolved in the electrolytic solution.

The lithium secondary cell using the electrode according to the invention is not particularly limited in structure

although it is generally comprised of a positive electrode, a negative electrode, an optional separator, and a gel electrolyte or electrolytic solution and applicable to sheet-shaped batteries and cylindrical batteries. It is noted that liquid electrolytes can be used as the electrolyte although the use of solid polymer electrolytes is especially preferred. In this case, the above-described fluorinated rubber polymeric resins such as P(VDF-CTFE) are preferably used as the polymer of the gel electrolyte.

It is also acceptable to use the electrode of the invention as one electrode while the other electrode is constructed from a commonly used collector. As the collector in this embodiment, it is a common practice to use aluminum etc. for the positive electrode and copper, nickel, etc. for the negative electrode. The collector may be either a foil or a mesh (or grid).

The electrode of the invention is also useful in electric double-layer capacitors.

In the electric double-layer capacitors, a gel solid electrolyte containing an electrolytic solution is preferably used in addition to polarizable electrodes as described above. The electrolytic solution is preferably of organic solvents. It is especially preferred to use polymeric electrolytes and in this case, the P(VDF-CTFE) according to the invention can also be used as the polymer of the gel electrolyte.

Included in the electrolyte salt are  $(C_2H_5)_4NBF_4$ ,  $(C_2H_5)_3CH_3NBF_4$ , and  $(C_2H_5)_4PBF_4$ .

The organic solvent may be selected from well-known various solvents, preferably electrochemically stable non-aqueous solvents such as propylene carbonate, ethylene carbonate,  $\gamma$ -butyrolactone, acetonitrile, N,N-dimethylformamide, 1,2-dimethoxyethane, sulfolane and nitromethane, alone or in admixture.

In the electrolytic solution of such organic solvent, the electrolyte may have a concentration of about 0.1 to 3 mol/liter.

The structure of the electric double-layer capacitor in which the electrode of the invention is used is not critical. Usually a separator is interleaved between a pair of polarizable electrodes while electrode layers on the polarizable electrodes and the separator are impregnated with the electrolytic solution. An insulating gasket is disposed at the periphery of the polarizable electrodes and the separator. Such an electric double-layer capacitor may be any of the so-called coin, sheet and cylindrical types.

It is also acceptable to use the electrode of the invention as one electrode while the other electrode is constructed from a commonly used polarizable electrode. The collector in this embodiment may be conductive rubber such as conductive butyl rubber, or it may be formed by thermal spraying of metals such as aluminum and nickel or by attaching a metal mesh to one surface of the electrode layer.

#### EXAMPLE

Examples of the present invention are given below by way of illustration.

##### Example 1

###### Preparation of gel electrolyte source solution

A source solution was prepared by weighing a copolymer of poly(vinylidene fluoride) with hexafluoropropylene (P(VDF-HFP) KynarFlex 2801 by Elf Atochem, HFP proportion ~6 mol %, molecular weight  $M_w=380,000$ ) as the polymer, a solution of 1M  $LiClO_4$  in ethylene carbonate/propylene carbonate (EC:PC=3:1) as the electrolytic solution, and acetone as the solvent so as to give a weight

ratio of P(VDF-HFP):1M  $LiClO_4$ /propylene carbonate:acetone=3:7:5, agitating and mixing them in a homogenizer at room temperature to 50° C. for about 1 to 5 hours.

###### Preparation of gel electrolyte film

A film of gel electrolyte was prepared by applying the source solution onto a quartz substrate as a thin layer, followed by drying and peeling.

###### Preparation of gel electrode slurry

A slurry was prepared by mixing the source solution and graphite as the negative electrode active material in a weight ratio of 2:1, and dispersing at room temperature for 60 minutes by means of a magnetic stirrer.

###### Fabrication of battery

A porous metal member having a three-dimensional skeleton structure was furnished by dipping a urethane foam (HR-50 by Bridgestone K. K.) in a graphite slurry, followed by drying and solidification, thereby imparting conductivity to the foam. Copper plating of 100  $\mu m$  was applied to the foam, which was heated and burned at 500° C. for 10 minutes and then subjected to chemical reduction at 800° C. for 20 minutes. The resulting porous metal member had an average porosity of 95% and a mean maximum pore diameter of 500  $\mu m$ . It was cut to the predetermined dimensions, obtaining a collector.

To the collector, the electrode-forming slurry prepared above was applied so as to give a dry thickness of 0.2 mm by a doctor blade technique, and dried in a dry atmosphere to form a negative electrode. Separately, a positive electrode was prepared by mixing the gel electrolyte solution,  $LiCoO_2$  as the active material and acetylene black as the conductive aid in a weight ratio of 2:7.5:1.2, and agitating them into a slurry in the same manner as the above-described electrode slurry. As described in U.S. Pat. No. 5,470,357, a gel electrode composition membrane was prepared using the slurry, and bonded under heat and pressure to an aluminum grid of 60  $\mu m$  mesh.

The thus obtained positive electrode, gel electrolyte film and negative electrode were laid in order, obtaining a lithium secondary battery.

##### Comparative Example 1

A lithium secondary battery was fabricated as in Example 1 except that a copper grid of 60  $\mu m$  mesh was used as the collector.

##### Comparative Example 2

A lithium secondary battery was fabricated using a copper grid as the collector as in Comparative Example 1. As described in U.S. Pat. No. 5,470,357, a gel electrode composition membrane was prepared before it was bonded under heat and pressure to the copper grid.

##### Comparative Example 3

A lithium secondary battery was fabricated as in Example 1 except that a copper foil was used as the collector.

##### Comparative Example 4

A lithium secondary battery of the electrolytic solution system was fabricated using the negative electrode material used in Example 1 as the negative electrode, the positive electrode material used in Example 1 as the positive electrode, and the solution of 1M  $LiClO_4$  in ethylene carbonate/propylene carbonate (EC:PC=3:1) used in Example 1 as the electrolytic solution.



The lithium batteries thus obtained were examined for direct printing or coating of the gel electrode slurry, initial capacity, and capacity retention after 30 cycles. The results are shown in Table 1.

TABLE 1

	Direct printing or coating	Initial capacity (mAh/g)	Capacity retention after 30 cycles (%)
E1	OK	123	90
CE1	NO	—	—
CE2	—	121	80
CE3	NO	—	—
CE4	—	120	90

## Example 2

A lithium battery was fabricated as in Example 1 except that a copolymer having a backbone consisting of vinylidene fluoride and chlorofluoroethylene and a poly(vinylidene fluoride) on a side chain ((P(VDF-CTFE), Sefral Soft G180F100 by Central Glass K. K., CTFE proportion ~15 mol %, molecular weight Mw=120,000) was used as the polymer.

## Comparative Examples 5-8

In Example 2, the same procedures as in Comparative Examples 1 to 4 were carried out. These are Comparative Examples 5 to 8.

The lithium batteries thus obtained were examined for direct printing or coating of the gel electrode slurry, initial capacity, and capacity retention after 30 cycles. The results are shown in Table 2.

TABLE 2

	Direct printing or coating	Initial capacity (mAh/g)	Capacity retention after 30 cycles (%)
E2	OK	125	90
CE5	NO	—	—
CE6	—	120	80
CE7	OK	118	60
CE8	—	122	90

## Example 3

A porous metal member was furnished by evaporating aluminum onto a urethane foam and heat treating the aluminum-deposited urethane foam for removing the urethane foam, leaving a porous aluminum member. A slurry was prepared by mixing the gel electrolyte source solution, LiCoO<sub>2</sub> as the positive electrode active material, and acetylene black as the conductive aid in a weight ratio of 2:7.5:1.2, and dispersing at room temperature for 30 minutes to 3 hours by means of a magnetic stirrer. As in Example 1, the slurry was applied to the porous aluminum member and dried, obtaining a positive electrode.

A battery was fabricated as in Example 1 with substitution of this positive electrode for the positive electrode of Example 1 and examined as in Example 1, finding further improvements in initial capacity and capacity retention.

## Example 4

A polarizable electrode and a gel electrolyte were prepared as in Example 1, but using activated carbon having a

specific surface area of 1,500 to 2,000 m<sup>2</sup>/g as the active material, propylene carbonate as the electrolytic solution, and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub> as the electrolyte salt, and changing the shape of the collector and gel electrolyte to conform to the 2016 type. They were received in a 2016 type coin-shaped cell, constructing an electric double-layer capacitor.

The electric double-layer capacitor thus obtained was subjected to a charge/discharge test between 0 V and 2 V, finding favorable characteristics. When the capacitance per gram of activated carbon was measured, a capacitance of 30 F/g was marked.

## BENEFITS OF THE INVENTION

As described above, the present invention provides an electrode capable of increasing the retaining force of a gel electrolyte component to a collector for enabling direct coating of the gel electrolyte component to the collector and thus featuring improved mass productivity and a reduced cost as well as a lithium secondary battery and an electric double-layer capacitor using the electrode.

What is claimed is:

1. An electrode comprising a porous metal member in sheet form having a 3-dimensional reticulated skeleton structure and a coating comprising a solid polymer electrolyte and an active material, wherein said porous metal member has a porosity of 80 to 98% and mean maximum pore diameter of 100 to 800 μm.

2. The electrode of claim 1 wherein said solid polymer electrolyte comprises a gelled polymer matrix containing an electrolytic solution.

3. A lithium secondary battery comprising the electrode of claim 1.

4. The lithium secondary battery of claim 3, further comprising an electrolyte comprising at least one electrolyte salt selected from the group consisting of LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiSO<sub>3</sub>CF<sub>3</sub>, and (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NLi.

5. The electrode of claim 1, wherein said porous metal member comprises at least one metal selected from the group consisting of Cu, Ni, Al, Fe, Cr, Zn, Sn, Pb, Ag, Cd, Co, Au, and Pt.

6. The electrode of claim 1, wherein said porosity is 90 to 95%.

7. The electrode of claim 1, wherein said mean maximum pore diameter is 250 to 500 μm.

8. The electrode of claim 1, wherein said porous metal member has a thickness of 0.1 to 3 mm.

9. The electrode of claim 1, wherein said porous metal member has a thickness of 0.4 to 0.6 mm.

10. The electrode of claim 1, wherein said solid polymer electrolyte comprises a chemically crosslinked gel obtained by polymerizing a photopolymerizable acrylate ethylene oxide with a polymer selected from the group consisting of a polyfunctional acrylate, polyfunctional polyacrylonitrile, polyfunctional polyethylene oxide, and polyfunctional polypropylene oxide.

11. The electrode of claim 1, wherein said solid polymer electrolyte comprises at least one polymer selected from the group consisting of polyvinylidene fluoride, a vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-chlorotrifluoroethylene copolymer, a vinylidene fluoride-hexafluoropropylene fluoro-rubber, a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene fluoro-rubber, and a vinylidene fluoride-tetrafluoroethylene-perfluoroalkyl vinyl ether fluoro-rubber.

12. The electrode of claim 1, wherein said solid polymer electrolyte comprises at least one non-aqueous solvent selected from the group consisting of ethylene carbonate,

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propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, 4-methyldioxolane,  $\gamma$ -butyrolactone, sulfolane, 3-methylsulfolane, dimethoxyethane, diethoxyethane, 5 ethoxymethoxyethane, and ethyldiglyme.

13. The electrode of claim 1, wherein said active material comprises at least one material selected from the group consisting of carbon, lithium metal, lithium alloy, and lithium oxide.

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14. The electrode of claim 13, wherein said carbon is selected from the group consisting of natural graphite, artificial graphite, a resin fired carbon material, and carbon fibers.

15. The electrode of claim 14, wherein said graphite has a mean particle size of 1 to 30  $\mu\text{m}$ .

16. The electrode of claim 13, wherein said lithium oxide is selected from the group consisting of  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiV}_2\text{O}_4$ .

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,280,878 B1  
DATED : August 28, 2001  
INVENTOR(S) : Satoshi Maruyama et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

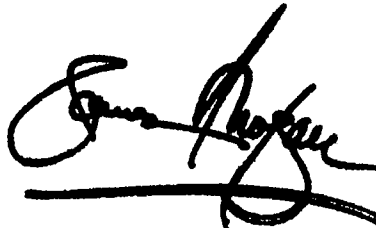
Title page.

Delete Item [54] in its entirety and replace with -- [54] **ELECTRODE, AND  
LITHIUM SECONDARY BATTERY AND ELECTRIC DOUBLE-LAYER  
CAPACITOR USING THE ELECTRODE --.**

Signed and Sealed this

Eleventh Day of June, 2002

Attest:

A handwritten signature in black ink, appearing to read "James E. Rogan", with a horizontal line drawn underneath it.

Attesting Officer

JAMES E. ROGAN  
Director of the United States Patent and Trademark Office

# EXHIBIT F



US005522127A

**United States Patent** [19]**Ozaki et al.**[11] **Patent Number:** **5,522,127**[45] **Date of Patent:** **Jun. 4, 1996**[54] **METHOD OF MANUFACTURING A  
NON-AQUEOUS ELECTROLYTE  
SECONDARY CELL**[75] **Inventors:** **Yoshiyuki Ozaki; Hizuru Koshina,**  
both of Neyagawa, Japan[73] **Assignee:** **Matsushita Electric Industrial Co.,  
Ltd., Osaka, Japan**[21] **Appl. No.:** **386,635**[22] **Filed:** **Feb. 10, 1995**[30] **Foreign Application Priority Data**

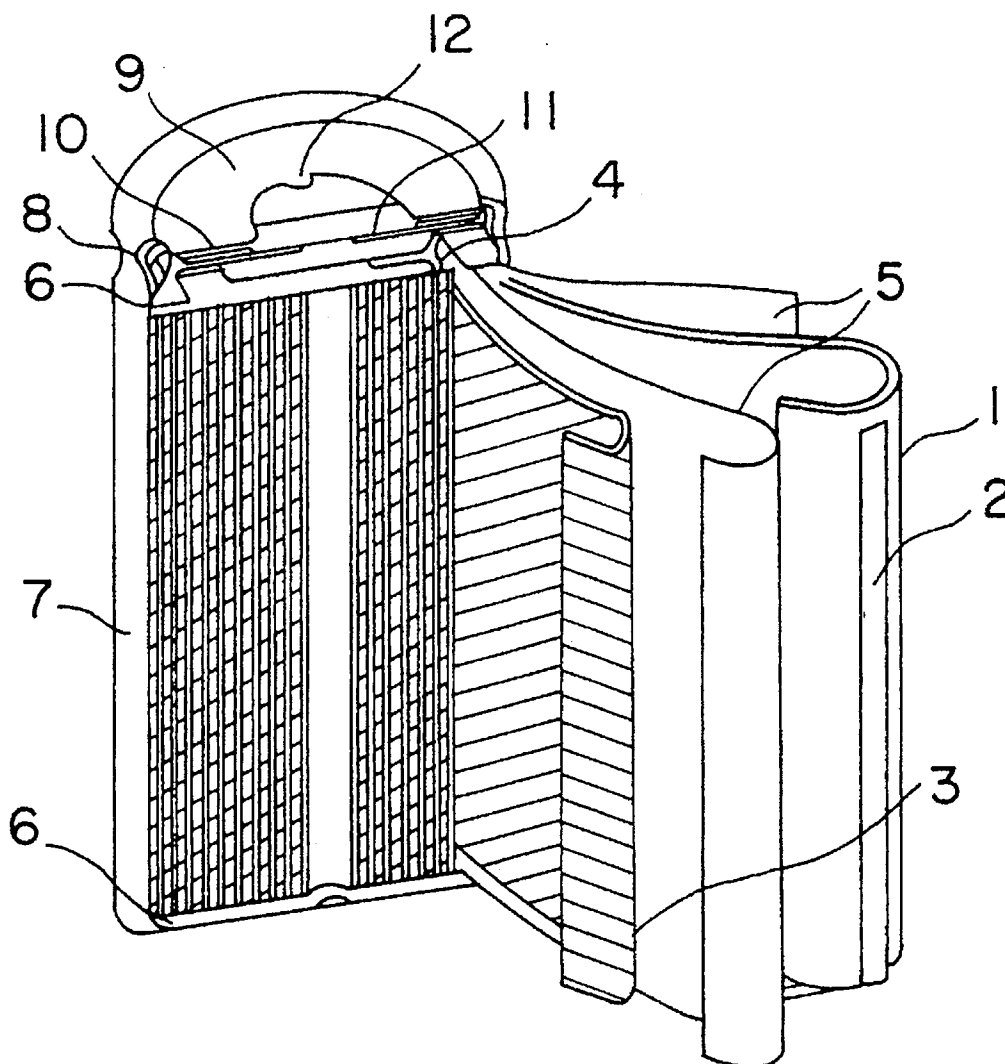
Feb. 10, 1994 [JP] Japan ..... 6-016338

[51] **Int. Cl.<sup>6</sup>** ..... **H01M 6/00**[52] **U.S. Cl.** ..... **29/623.5; 29/623.1; 264/29.1;  
264/105**[58] **Field of Search** ..... **29/623.1, 623.5;  
264/105, 29.1**[56] **References Cited****U.S. PATENT DOCUMENTS**4,161,063 7/1979 Goebel et al. .... 29/623.5  
4,883,617 11/1989 Benn et al. .... 264/29.1  
5,344,724 9/1994 Ozaki et al. .... 429/94**FOREIGN PATENT DOCUMENTS**

1-290559 11/1989 Japan .

*Primary Examiner*—Kathryn Gorgos*Attorney, Agent, or Firm*—Ratner & Prestia[57] **ABSTRACT**

A non-aqueous electrolyte secondary cell having high charging efficiency over wide temperature range including low temperature, high energy density and superior charge and discharge cycle life, provided with a negative electrode manufactured with mesophase graphite particles obtained by a process to carbonize and then fully graphitize with pulverizing process added before or after the carbonization.

**10 Claims, 1 Drawing Sheet**

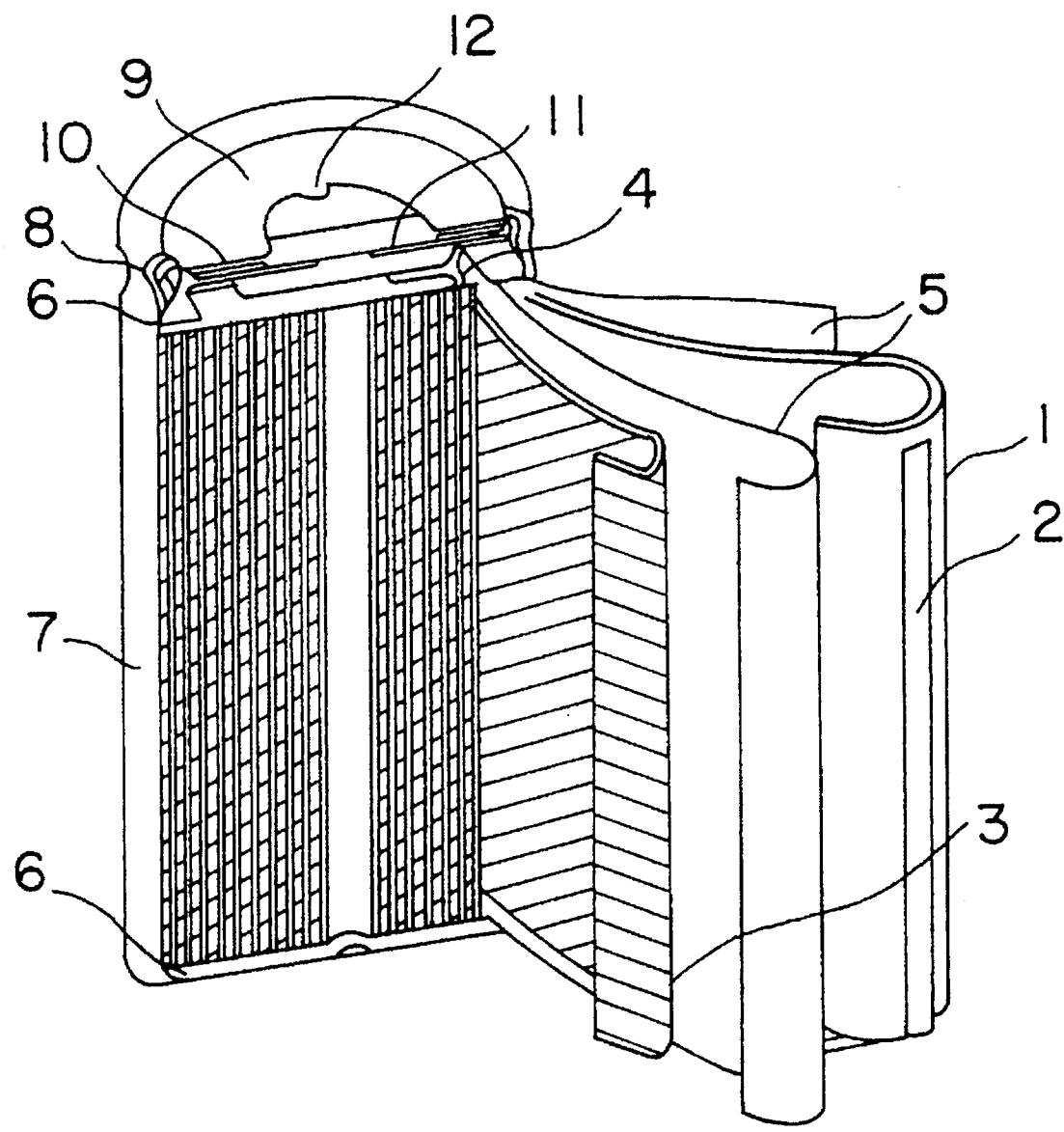


FIG. 1

# METHOD OF MANUFACTURING A NON-AQUEOUS ELECTROLYTE SECONDARY CELL

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to a non-aqueous electrolyte secondary cell and a method of manufacturing the same, the cell having a negative electrode of carbon material to which intercalation by charging and deintercalation by discharging of lithium are possible.

### 2. Description of the Prior Art

In recent years, electronic appliances have become more and more portable or cordless. In such circumstances, demand for the development of secondary cells which are smaller, lighter and of higher energy density by manufacturers of such appliances are increasing.

Non-aqueous secondary cells with negative electrodes of metallic lithium or lithium alloy can produce high voltages and high energy densities and, hence, research and development of these various types of battery systems have been active. However, it was found that discharging capacity decreases as charging and discharging are repeated in cells with negative electrodes made of metallic lithium which seems to be capable of producing the highest voltages and highest energy densities.

The decreasing discharging capacity is likely due to internal short circuiting of the cell by dendritic metallic lithium deposited on the negative electrode or side reactions of the decomposition of the organic solvent in the non-aqueous electrolyte. Also, such cells were insufficient in high-rate charging and discharging characteristics and in over-discharging durability, and the application in other fields was considered difficult. Further, suspicions of poor safety of cells having negative electrodes produced of metallic lithium or lithium alloy were big obstacles for putting them to practical use.

Thus, instead of negative electrodes of metallic lithium or lithium alloy, a new type of negative electrode material has been discovered which utilizes intercalation and deintercalation reaction of lithium by charging and discharging.

Among them, using carbon material as the negative electrode has been produced. Carbon material has nearly the same characteristic as metallic-lithium used in negative-electrode. For example, see U.S. Pat. No. 4,423,125. And, it has been reported in research that carbon materials are capable of intercalating or deintercalating more lithium by charging and discharging thereby obtaining negative electrodes of higher capacity.

Of the reports, two main themes are seen: one argues that highly graphitized carbon materials, such as natural graphite or artificial graphite are suitable; the other reports pseudographite materials such as those obtained by carbonization of hydrocarbons or polymer materials at temperatures as low as 1000° to 1500° C. are suitable.

In both cases, various points have been discussed, e.g., the effects of using different kinds of precursor carbon, the methods and condition of carbonization and graphitization. Interplanar spacing values of (002) plane or crystal thickness along the c axis or a axis obtained by X-ray powder diffraction for carbon materials have been reported.

It has been known that the quantity of lithium in the intercalation compound which has been formed by intercalation between layers of graphite is at a maximum when it

has the form of  $C_6Li$ . The specific capacity of graphite at this case being 372 mAh/g.

However, a pseudographite material with low graphitization has a low quantity of intercalated lithium, so that the specific capacity is as low as 200 mAh/g, limiting the capacity of the cell.

In order to solve the above problems and to obtain high capacity, a method has been proposed and described in U.S. Pat. No. 5,344,724 by some of the inventors of the present invention. According to that method, pitch is melted to produce mesophase carbon micro beads, which are the intermediate products between liquid phase and solid phase, the beads are then carbonized and then graphitized to become mesophase graphite and are then used as the negative electrode material. By using mesophase graphite particle for the negative electrode, the quantity of intercalated lithium is increased, resulting in the increased specific capacity of the negative electrode. However, when negative electrodes are prepared by coating core foils of copper or stainless steel (which are to become collectors) on both the surfaces with paste composed of the mesophase graphite particles and a binder; drying the electrodes; pressing the electrodes by a roller, and simultaneously fabricating cells, the cells were found to have the quantity of lithium intercalated in the mesophase graphite particles greatly reduced when they are charged at temperatures below 0° C., compared with at ordinary temperatures. The lithium which was not intercalated was deposited on the negative electrode surface in a metallic dendritic form. The metallic lithium, once deposited as dendrite, is not extinguished when the charging and discharging are repeated, resulting in no contribution to the main reaction, and a decrease in the cell capacity. Such cells do not recover discharge capacity if they are then put into ordinary temperatures. Furthermore, these cells short circuit internally due to the metallic dendritic lithium and have a short charging and discharging cycle life. Such deposition of metallic lithium and decrease of cell capacity are not observed if the charge and discharge cycle are performed at ordinary temperatures.

The above described deterioration by charging and discharging at a low temperatures likely results from the basal plane of the graphite crystal becoming parallel to the core foil surface due to high orientation characteristics of the mesophase graphite. It has been found that at the surface perpendicular to the basal plane of the graphite crystal lithium is easily intercalated; whereas, in the above described negative electrode, the planes to which lithium is to be intercalated are arranged almost perpendicular to the negative electrode surface. This leads to the checking of lithium easily intercalated between the graphite layers during charging.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide non-aqueous electrolyte secondary cells of high energy-density with negative electrodes of carbon material to which lithium is intercalated and deintercalated by charging and discharging. The secondary cells provide long charging and discharging cycle lives and superior recoverability capacities by preventing the deposition of dendritic metallic lithium. The deposition of metallic lithium causes the capacity loss of cells when charged at low temperatures to suppress internal short circuiting and decreases of discharge capacities.

To attain the above object, a non-aqueous electrolyte secondary cell according to the present invention has a

negative electrode made from mesophase graphite particles. The mesophase graphite particles are produced by starting with micro beads of mesophase carbon made from pitch (coal-tar pitch, petroleum pitch etc.) and either pulverizing them to fine particles first and then by carbonizing and graphitizing, or carbonizing them first and then pulverizing and graphitizing:

According to the present invention, the negative electrode is formed by pressing the mesophase graphite particles which were obtained by adding a pulverizing process before or after carbonizing a core foil; the orientations of the carbon crystals are distributed randomly. This leads to smooth intercalating of lithium at charging over a wide temperature range resulting in an increased cell capacity.

#### BRIEF EXPLANATION OF THE DRAWING

FIG. 1 shows a cross-section and broken perspective view of non-aqueous electrolyte cylindrical secondary cell according to the present invention.

#### DETAILED EXPLANATION OF THE INVENTION

Referring to the drawings, an exemplary example of the present invention is explained as follows.

##### (1) Preparation of mesophase carbon micro beads;

Pitch (coal-tar, or petroleum pitch) was heated and melted; mesophase carbon micro beads were separated on a centrifuge from the pitch matrix, and classified according to particle size.

##### (2) Preparation of mesophase graphite particles;

A) Mesophase carbon micro beads of 20  $\mu\text{m}$  average diameter were pulverized by a jet mill to smaller particles of 5.7  $\mu\text{m}$  average diameter; the pulverized beads were then carbonized at 1000° C. and further graphitized at 2800° C. to obtain mesophase graphite particles A, which had 5.7  $\mu\text{m}$  average diameter and their specific surface area was 3.2  $\text{m}^2/\text{g}$ .

B) Mesophase carbon micro beads of 20  $\mu\text{m}$  average diameter (the same as that in A) were first carbonized at 1000° C., and then pulverized on a jet mill to 5.8  $\mu\text{m}$  average diameter; the pulverized beads were further graphitized at 2800° C. to obtain mesophase graphite particles B having 5.8  $\mu\text{m}$  average diameter and specific surface area 3.4 of  $\text{m}^2/\text{g}$ .

C) Mesophase carbon micro beads of 20  $\mu\text{m}$  average diameter (same as that in A) were carbonized at 1000° C., and then graphitized at 2800° C.; the graphitized beads were then pulverized by a jet mill to 6.0  $\mu\text{m}$  average diameter to obtain mesophase graphite particles C for comparison having specific surface area of 12.5  $\text{m}^2/\text{g}$ .

D) Mesophase carbon micro beads of 30  $\mu\text{m}$  average diameter were pulverized to 12  $\mu\text{m}$  average diameter, and then carbonized and graphitized at the same temperatures as above to obtain comparison mesophase graphite particles D.

E) Mesophase carbon particles of 5.7  $\mu\text{m}$  average diameter were directly carbonized and graphitized at the temperature as above in A using a conventional method, to obtain mesophase graphite particles E of 5.7  $\mu\text{m}$  average diameter and 3.0  $\text{m}^2/\text{g}$  specific surface area.

F) According to a conventional method, mesophase carbon particles of 20  $\mu\text{m}$  average diameter were pulverized to 5.7  $\mu\text{m}$  average diameter; carbonized at 1000°

C. and graphitized at 2300° C., (which is lower than that in A), to obtain mesophase graphite particles E, —which represents another example in the prior art corresponding to pseudographite.

##### (3) Fabrication of the negative electrode plate:

A hundred weight part of each of the mesophase graphite particles obtained as above was mixed with 5 parts by weight styrene butadiene rubber, and then after the addition of carboxymethyl cellulose (CMC) aqueous solution, mixed to obtain a paste. A copper foil of 0.02 mm thickness was coated with this paste on both surfaces, and, after drying, the foil covered with paste was pressed by a roller to 0.20 mm thickness. A negative electrode plate 39 mm wide and 260 mm long was cut from the rolled foil.

##### (4) Fabrication of positive electrode plate:

A hundred weight part of lithium cobaltate ( $\text{LiCoO}_2$ ) powder, 3 parts by weight of acetylene black as an electro-conductive agent, and 7 parts by weight of poly-tetrafluoro ethylene as a binder were mixed together, CMC aqueous solution was then added, to obtain a paste. Aluminum foil of 0.03 mm thickness was coated on both sides with this paste; dried and pressed by a roller to 0.18 mm thickness. A positive electrode plate 37 mm wide and 240 mm long was cut from the rolled foil.

##### (5) Fabrication of experimental cells:

The positive and negative electrode plates were each provided with a lead plate. A separator formed of microporous polyethylene membrane 0.025 mm thick, 45 mm wide and 730 mm long was sandwiched between these electrode plates. The positive and negative electrode plates and the separator were wound together to form an electrode plate group. The electrode plate group was placed in a cell case, to which a non-aqueous electrolyte was poured. By sealing, a AA size cell was fabricated. FIG. 1 shows a detailed broken perspective view of the non-aqueous electrolyte secondary battery, in which numeral 1 is a negative electrode plate with a lead plate 2, and numeral 3 is a positive electrode plate with a lead plate 4. An electrode plate group formed by the negative electrode plate 1 and positive electrode plate 3 wound together with a separator 5 in between is placed in a cell case 7 with insulators 6 thereon and thereunder. The cell case 7 works as the negative terminal. The cell case 7 is sealed at the upper flange with a cover 9 with a gasket 8 in between. The cover 9 comprises a positive temperature coefficient thermister (PTC) device 10 to prevent over current through outer short circuiting with, for example, a safety valve 11 and exhaust hole 12. The negative electrode lead plate 2 and positive electrode lead plate 4 are connected with the inside bottom of the cell case 7 and the cover 9, respectively. The non-aqueous electrolyte used was an organic electrolyte prepared by dissolving  $\text{LiPF}_6$  (1 mol/l) in a mixed solvent of ethylene carbonate, diethyl carbonate and methyl propionate in a 3:5:2 volume ratio.

##### (6) Charging and discharging test;

The cells prepared as above and designated A, B, C, D, and E according to the designation of mesophase graphite particles of the negative electrodes which were tested for charging and discharging performance. The test conditions were; charging was carried out for two hours, initially with 350 mA constant current, and, once the set voltage 4.1 V was obtained, the voltage was kept constant and the discharging was continued with constant current of 500 mA until an end



voltage of 3.0 V was reached. The charging and discharging were repeated for 20 cycles under the above condition and at 20° C., and then, after keeping the cell for 6 hours at a temperature of 0° C., 20 cycles of charging and discharging were applied. Then, after the last discharging, the environmental temperature of the cell was returned to 20° C., and after 6 hours of keeping the cell at a temperature of 20° C. 50 charging and discharging cycles were repeated.

In the course of testing, last Initial capacity, 0° C. capacity, Recovery Capacity, and Last capacity were measured; wherein "Initial capacity" means the discharge capacity at the 10th cycle in the charging and discharging cycles at 20° C., "0° C. capacity" means the discharge capacity at the third cycle in the charging and discharging cycles at 0° C., "Recovery capacity" means the discharge capacity at the third cycle in the charging and discharging cycles after returning to 20° C., and "Last capacity" means the discharge capacity at the fiftieth discharge after the returning to 20° C.

Based on these measurements, 0° C.—capacity retention ratio and Recovery Capacity ratio were calculated by the following formulae:

$$0^{\circ}\text{C.} - \text{Capacity Retention Ratio (\%)} = \frac{0^{\circ}\text{C.} - \text{capacity}}{\text{Initial capacity}} \times 100$$

$$\text{Recovery Capacity Ratio (\%)} = \frac{\text{Recovery capacity}}{\text{Initial capacity}} \times 100$$

The results are shown in the Table.

TABLE I

Cells	Initial capacity (mAh)	Or capacity retention ratio (%)	Capacity recovery ratio (%)	Last capacity (mAh)
A (Invented)	520	76.2	100.0	519
B (Invented)	523	75.2	100.0	521
C (Comparison)	435	62.0	92.0	358
D (Comparison)	510	72.3	98.7	397
E (Prior art)	524	56.5	88.5	412
F (Comparison)	488	76.8	100.0	431

In Table I, it is observed that cells A and B according to the present invention have the high capacities, superior 0° C.—capacity retention ratios, 100% capacity recovery ratios, and the Last capacities not significantly different from the Initial capacities, so that deterioration of capacities by the charging and discharging cycle was not recognized. The cells were dismantled after the charge and discharge test and the negative electrodes were observed to find any significant changes of shape or deposition of dendritic metallic lithium.

The cell C, for comparison, (having mesophase graphite particles in the negative electrode prepared by pulverizing after graphitization so as to have the same average size as that in A and B) had an Initial capacity as low as 435 mAh. Also, cell C had a low 0° C.—capacity retention ratio, capacity recovery ratio and Last capacity. After the charge and discharge test, a little amount of deposited dendritic metallic lithium was observed on the negative electrode. It is presumed that the large specific surface area of the mesophase graphite particles for cell C lead to a side reaction which decomposes the organic solvent in the non-aqueous electrolyte and further decreases the capacity.

As for the cell D, for comparison, although it had an Initial capacity, 0° C.—capacity retention ratio and capacity recovery ratio not significantly different from those of invented cells A and B, the Last capacity was low and the deterioration of capacity by the charging and discharging cycle was significant. Observing the negative electrode of the dismantled cell D, there was no deposition of dendritic

metallic lithium observed, but, there was dendritic metallic lithium coming-off the negative electrode mix from the core foil. It seems that the mesophase graphite particles of the negative electrode in cell D had 12.5 μm average diameter, which was larger than those of the other cells. This resulted in difficult adherence of the particles onto the foil when fabricated and the particles became smaller in size due to expansion and shrinkage during the charging and discharging cycles which led to capacity deterioration.

The cell E manufactured according to conventional methods had the Initial capacity similar to those of invented cells A and B, but the 0° C. capacity, retention ratio, capacity recovery ratio and Last capacity were low and the deterioration of the capacity due to the charging and discharging cycles was significant. Almost all over the negative electrode surface of the dismantled cell, deposition of dendritic metallic lithium was observed. This phenomena is thought, as previously described, to be brought about by the significant decrease of the lithium quantity intercalatable into the mesophase graphite particles when charged at a low temperature.

The cell F, also of prior art, had the 0° C. —capacity retention ratio and the recovery ratio both satisfactory and little deterioration of capacity during the charging and discharging cycles, but, the Initial capacity is 30 to 40 mAh lower than those of cells A or B. It is deemed that a graphitization temperature as low as 2300° C. leads to imperfect graphitization which results in little lithium intercalated in the mesophase graphite particles and a low level of the capacity.

One object of the present invention is mesophase graphite particles produced by: carbonizing and graphitizing mesophase carbon micro beads, which were pulverized before or after the carbonization, to fine particles of about 6 μm average diameter and were suitable for pressing by a roller on a core foil. According to many inventor's investigations, favorable mesophase graphite particles were obtained from mesophase micro beads having average particle diameters in the range of 6 to 25 μm, preferably 10 to 20 μm. Also, it was confirmed that favorable mesophase graphite particles could be obtained if the average particle diameter attained by the pulverizing before or after the carbonization was within the range of 3 to 10 μm, preferably 5 to 7 μm. If the average particle diameter is less than 3 μm, an internal short circuiting is apt to happen, which, if not prevented by a PTC device, may result in a rapid heating, [and] explosion and/or fire. Average particle diameters over 10 μm, on the other hand, as explained referring to the cell D, cause a capacity decrease due to a coming-off of the negative electrode mixture as the charging and discharging cycle proceeds. Further, the favorable range of the specific surface area of the mesophase graphite particles is 1.0 to 8.0 m<sup>2</sup>/g, preferably 2.5 to 5.0 m<sup>2</sup>/g. If the specific surface area is less than 1.0 m<sup>2</sup>/g, the high-rate discharge characteristic and rapid-charging characteristic are inferior; while, over 8.0 m<sup>2</sup>/g, as explained previously referring to the cell C, the dendritic metallic lithium and the organic solvent in the non-aqueous electrolyte react to decompose the solvent to reduce the discharge capacity. The temperature for the carbonization of the mesophase carbon micro beads, which was 1000° C. for the above example, is in the range of 800° to 1300° C., preferably 900° to 1100° C. Also, the graphitization temperature, which was 2800° C. in the above explained example, is enough if it is in the range of 2400 to 3000° C., preferably 2600° to 2800° C. to obtain fully graphitized carbon materials.

The present invention is not confined to employing the positive electrode material and electrolyte composition as

described in the above examples. As for the positive electrode material, not only  $\text{LiCoO}_2$  but also  $\text{LiNiO}_2$ ,  $\text{LiFeO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and the like can be used, to which lithium can deintercalate and intercalate by charging and discharging.

As for the organic solvent of the organic electrolyte for the non-aqueous electrolyte, propylene carbonate (PC) is not employed, because it decomposes to generate a gas [at] during charging. On the other hand, ethylene carbonate (EC) used alone is not suitable, since it has a high melting temperature and is solid at ordinary temperature, though it has no unfavorable side reaction, as of PC. However, EC may be used in a mixed solvent of EC and either ether such as 1,2 dimethoxyethane, chain carbonate such as diethyl carbonate, ethyl methyl carbonate, or aliphatic-carboxylic acid ester such as methyl propionate, which are of low melting temperature and of low viscosity.

As described above in detail, the present invention provides a non-aqueous electrolyte secondary cells having a high charging efficiency over a wide temperature range, high energy densities, and superior charge-and-discharge-cycle-lives. The invention is achieved by employing in the negative electrodes mesophase graphite particles obtained by starting from mesophase carbon micro beads, and then either pulverizing and then carbonizing and graphitizing the beads, or carbonizing and then pulverizing and graphitizing the beads.

What is claimed:

1. A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary cell comprising the steps of preparing a paste containing mesophase graphite particles, said graphite particles prepared by carbonizing, graphitizing at a temperature of from  $2400^\circ$  to  $3000^\circ$  C. and pulverizing mesophase carbon micro beads to have an average particle diameter within a defined size range, said micro beads being pulverized before carbonizing or after carbonizing; coating both sides of a core foil with said paste; and drying and pressing said foil coated with paste.

2. A method of manufacturing an electrode according to

claim 1 including the step of pulverizing said mesophase graphite particles to have an average particle diameter in the range of 3 to  $10\text{ }\mu\text{m}$ .

3. A method of manufacturing an electrode according to claim 1 including the step of pulverizing said mesophase graphite particles to have an average particle diameter in the range of 5 to  $7\text{ }\mu\text{m}$ .

4. A method of manufacturing an electrode according to claim 1, including the step of selecting said mesophase carbon micro beads, to have an average diameter in the range of 6 to  $25\text{ }\mu\text{m}$  before pulverizing.

5. A method of manufacturing an electrode according to claim 1, including the step of selecting said mesophase carbon micro beads to have an average diameter of 10 to  $20\text{ }\mu\text{m}$  before pulverizing.

6. A method of manufacturing an electrode according to claim 1, including the step of selecting said mesophase graphite particles to have a specific surface area in the range of  $1.0$  to  $8.0\text{ m}^2/\text{g}$ .

7. A method of manufacturing an electrode according to claim 1, including the step of selecting said mesophase graphite particles to have a specific surface area in the range of  $2.0$  to  $5.0\text{ m}^2/\text{g}$ .

8. A method of manufacturing an electrode according to claim 1, including the step of carbonizing said mesophase carbon micro beads at a temperature of from  $800^\circ$  to  $1300^\circ$  C.

9. A method of manufacturing an electrode according to claim 1, including the steps of carbonizing said mesophase carbon micro beads at a temperature of from  $900^\circ$  to  $1100^\circ$  C., and graphitizing said carbonized mesophase carbon at a temperature of from  $2600^\circ$  to  $2800^\circ$  C.

10. A method of manufacturing an electrode according to claim 1 including the step of selecting said core foil from the group consisting of copper and stainless steel.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,522,127  
DATED : June 4, 1996  
INVENTOR(S) : Ozaki et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, item [57] Abstract, line 2, after "over" insert --a--.

On the title page, item [57] Abstract line 6, after "with" insert --a --.

Column 7, line 32, between "3000°C." and "and" insert a comma --,--.

Signed and Sealed this  
Fifteenth Day of October, 1996

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

# EXHIBIT G

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(54) **Gel electrolyte and cell using same**

(57) A fire-retardant gel electrolyte comprising a gelled solution composed of a non-aqueous solvent and a salt of an electrolyte dissolved in the non-aqueous solvent, the gel electrolyte having an ionic conductivity of 1 mS/cm at a temperature of 25° C. In addition, in accordance with the present invention, there is also provided a cell comprising a fire-retardant gel electrolyte having an ionic conductivity of 1 mS/cm or greater at a temperature of 25° C, and positive and negative electrodes.

## Description

BACKGROUND OF THE INVENTION

## 5 Field of the Invention:

This invention relates to a fire-retardant gel electrolyte which can be employed in a lithium-type secondary cell or the like instead of a non-aqueous electrolyte solution and a cell using the fire-retardant gel electrolyte.

## 10 Prior Art:

Recently, an intense attention has been paid to a lithium secondary cell which is composed of a positive electrode made of a lithium-containing compound, a negative electrode made of a material such as lithium, a lithium alloy and a carbonaceous material capable of occluding lithium, and a non-aqueous electrolyte solution composed of a non-aqueous solvent and a salt of an electrolyte dissolved in the non-aqueous solvent, because the lithium secondary cell exhibits a relatively large electromotive force (output) and a relatively high energy density as compared with aqueous electrolyte solution-type secondary cells such as a lead cell, a nickel-cadmium cell or the like.

In order to further improve a performance of such a lithium secondary cell, it is important to take into account a property of the electrolyte which gives an influence on an ionic conductivity between the positive and negative electrodes, in addition to selection of materials used for the negative positive electrodes. As a consequence, a variety of proposals concerning non-aqueous solvents and electrolyte salts has been made to obtain an electrolyte having a high ionic conductivity and an enhanced resistance to a high voltage.

For example, the non-aqueous solvent used conventionally includes a carbonate-series solvent such as propylene carbonate, ethylene carbonate, methyl-ethyl carbonate and dimethyl carbonate,  $\gamma$ -butyl lactone, 1, 2-dimethoxy ethane, methyl propionate, butyl propionate and the like.

Further, the electrolyte salt reported and used conventionally includes  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiAsF}_6$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiC}(\text{CF}_2\text{SO}_2)_3$ , or the like.

However, the non-aqueous electrolyte solution composed of the non-aqueous solvent and the electrolyte salt enumerated above has a relatively small heat capacity, as described in Japanese patent laid-open publication No. 184870/92. As a result, in the event that the cell is accidentally placed in the flame, the solvent is caused to be evaporated in association with an increase of the ambient temperature, so that there is a risk that the solvent vapor fires.

One measure for preventing the above-mentioned problem has been proposed in Japanese patent laid-open publication No. 184870/92 in which a fire-retardant phosphoric acid ester is added to the electrolyte solution to eliminate the possible firing.

However, an organic ester compound such as phosphoric acid ester has such a problem that an electrochemical resistance to an oxidation/reduction reaction is relatively small. If such phosphoric acid ester is applied to a lithium secondary cell having an advantageously high terminal voltage, for example, 4 volts or higher, phosphoric acid ester is subjected to an undesired oxidation/reduction reaction in association with repeated charging and discharging cycles, which results in deterioration of a discharging capacity of the cell.

40 OBJECT AND SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a gel electrolyte suitably applicable as an electrolyte material for a cell and having an excellent fire-retardant property and an enhanced electrochemical resistance to an oxidation/reduction reaction.

Further, it is another object of the present invention to provide a cell exhibiting an excellent discharge capacity, in which the above-mentioned fire-retardant gel electrolyte is used.

In order to accomplish the above-mentioned objects, in accordance with one aspect of the present invention, there is provided a fire-retardant gel electrolyte comprising a gelled solution composed of a non-aqueous solvent and an electrolyte salt dissolved in the non-aqueous solvent, the gel electrolyte having an ionic conductivity of 1 mS/cm or greater at a temperature of 25° C.

Further, in accordance with another aspect of the present invention, there is provided a cell comprising a fire-retardant gel electrolyte having an ionic conductivity of 1 mS/cm or greater at a temperature of 25° C, and positive and negative electrodes.

It has been found that, when a non-aqueous electrolyte solution having a particular composition is gelled by using, for example, a polymer having a side chain to which a nitrile group is bonded, a fire-retardant gel electrolyte having as high an ionic conductivity as 1 mS/cm or greater at a temperature of 25° C can be obtained.

The fire-retardant gel electrolyte obtained according to the present invention has an ionic conductivity of 1 mS/cm or greater and does not contain the material exhibiting a deteriorated resistance to an oxidation/reduction reaction, such

as phosphoric acid ester, so that such a fire-retardant gel electrolyte is suitably employed as an electrolyte material for a cell. Specifically, when the gel electrolyte is applied to the production of the cell, the resultant cell exhibits an excellent fire-retardant property by which a possible firing accident can be eliminated even when the cell is placed in the flame, so that a cell having a high safety can be obtained. In addition, when the gel electrolyte is used as an electrolyte material for a cell, any leakage of the gel electrolyte from the cell is eliminated even when handled roughly, so that a contamination of devices to which the cell is mounted can be prevented.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ternary composition diagram showing a preferred range for a fire-retardant gel electrolyte according to the present invention.

Fig. 2 is a schematic diagram showing a testing procedure for examining a fire-retardant property of a gel electrolyte according to the present invention.

Fig. 3 is a sectional view of a cell according to one preferred embodiment of the present invention, to which a fire-retardant gel electrolyte according to the present invention is applied.

Fig. 4 is a graph showing a characteristic curve of a discharging property of a primary cell to which the fire-retardant gel electrolyte according to the present invention is applied.

Fig. 5 is a graph showing a characteristic curve of a charging and discharging properties of a secondary cell to which the fire-retardant gel electrolyte according to the present invention is applied.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is basically concerned with a fire-retardant gel electrolyte which is produced by gelling a non-aqueous electrolyte solution having a particular composition by using a polymer, for example, those having a side chain to which at least one nitrile group is bonded, and a cell produced by using such a fire-retardant gel electrolyte. The fire-retardant gel electrolyte obtained can exhibit an ionic conductivity as high as 1 mS/cm or greater at a temperature of 25° C.

As mentioned above, such a fire-retardant gel electrolyte has an ionic conductivity of 1 mS/cm or greater and does not contain a material causing the deterioration in a resistance to an oxidation/reduction reaction, so that it is possible to employ the fire-retardant gel electrolyte as an electrolyte material for the production of a cell. When the fire-retardant gel electrolyte is used as the electrolyte material for the production of cells, the resultant cell can exhibit an excellent fire-retardant property and an enhanced safety whereby possible firing of the cell is effectively prevented, for example, even when it is accidentally placed in the flame. In addition, no leakage of the gel electrolyte occurs even when handled roughly so that the contamination of devices to which the cell is mounted is effectively prohibited.

In the production of such a fire-retardant gel electrolyte, an electrolyte solution having the particular composition can be converted to a gel state by using a gelling agent, for example, a polymer having a side chain to which at least one nitrile group is bonded.

Specifically, when the electrolyte solution is gelled by the polymer having a side chain to which at least one nitrile group is bonded, a non-aqueous electrolyte solution composed of a predetermined amount of an electrolyte salt and a non-aqueous solvent is preliminarily prepared. After heating, a gelling agent, namely the polymer having a side chain to which at least one nitrile group is bonded, is added to the non-aqueous electrolyte solution. The addition of the gelling agent causes an increase in viscosity of the non-aqueous electrolyte solution. After completely dissolving the gelling agent in the non-aqueous electrolyte solution, the resultant gel solution is immediately stretched over a substrate and then gradually cooled to obtain the fire-retardant gel electrolyte.

The gelling agent, namely the polymer having a side chain to which at least one nitrile group is bonded, is preferably polyacrylonitrile in view of its gelling state and fire retardant property. Further, the gelling agent may be in the form of a copolymer which is obtained by copolymerizing a mixture containing an acrylonitrile monomer and other monomers in an appropriate proportion. Examples of such an acrylonitrile-series copolymer may include an acrylonitrile-butadiene rubber, an acrylonitrile-butadiene-styrene resin, an acrylonitrile-polyethylene chloride-styrene resin, an acrylonitrile-styrene resin, an acrylonitrile-ethylene-propylene-diene-styrene resin, an acrylonitrile-vinyl chloride resin, an acrylonitrile-methacrylate resin, or the like.

Here, it should be noted that a degree of the gelation of the non-aqueous electrolyte solution is determined by a molecular weight of the polyacrylonitrile and the acrylonitrile-series copolymer used as the gelling agent. Accordingly, it is necessary that each of the polyacrylonitrile and the acrylonitrile-series copolymer has such a molecular weight that a sufficient gelation is caused thereby. However, when the molecular weight of the gelling agent is extremely large, the viscosity of the non-aqueous electrolyte solution is too high when added, so that the film formation or stretching of the gel electrolyte on the substrate becomes difficult. In view of easiness of the film formation, it is preferred that the polyacrylonitrile or the acrylonitrile-series copolymer has a number-average molecular weight ranging from about 50,000 to about 500,000.

The non-aqueous solvent and the electrolyte salt used for the production of the gel electrolyte may be those generally used for the production of a lithium secondary cell.

Examples of the suitable non-aqueous solvent may include those having an electric potential window ranging from -0.3 V to 4.9 V relative to an electric potential of lithium. Particularly, ethylene carbonate (EC), propylene carbonate (PC),  $\gamma$ -butyl lactone or the like is preferable because an electric potential window of those compounds is fallen within the above mentioned range and can impart a high ionic conductivity to the gel electrolyte. Incidentally, these non-aqueous solvents are used singly or in the form of a mixture of a plurality of compounds. A particularly preferable example of the non-aqueous solvent for the gel electrolyte is a mixture containing ethylene carbonate (EC) and propylene carbonate (PC) in combination.

One of preferred examples of the electrolyte salt may include  $\text{LiPF}_6$  because it exhibits an excellent ionic conductivity and can impart a high fire-retardant property to the resultant gel product. Although  $\text{LiPF}_6$  may be combined with the other lithium salt, it is preferred that  $\text{LiPF}_6$  is used singly.

Incidentally, the optimum proportions of these materials used are determined by taking into account easiness of the film formation and a degree of the gelation in addition to the ionic conductivity and the fire-retardant property. Concretely, when the polyacrylonitrile is used as the gelling agent, a molar ratio of a monomer as a repeating unit of the polyacrylonitrile to the non-aqueous solvent is suitably in the range of 5:95 to 30:70 though it varies depending upon kinds of the non-aqueous solvent, the gelling agent and the electrolyte salt used therein.

Particularly, when polyacrylonitrile is used as the gelling agent and a mixture of ethylene carbonate (EC) and propylene carbonate (PC) is used as the non-aqueous solvent, it is preferred that the ratio between the monomer as the repeating unit of polyacrylonitrile, ethylene carbonate (EC) and propylene carbonate (PC) is fallen within a region surrounded by the lines between four sites A, B, C and D of a ternary composition diagram as shown in Fig. 1.

When the proportion of acrylonitrile monomer is smaller than those of the region, the gelation of the non-aqueous electrolyte solution cannot proceed satisfactorily so that a gel electrolyte having a good quality cannot be obtained. On the other hand, when the proportion of acrylonitrile is greater than those values of the region, there is a tendency that a good film formation of the resultant gel electrolyte cannot be achieved. Meanwhile, since the ionic conductivity of the gel electrolyte varies depending upon an amount of polyacrylonitrile added, the ionic conductivity of the fire-retardant gel electrolyte can be adjusted to an optimum value by controlling the proportion of polyacrylonitrile to be added to the mixture of the non-aqueous solvent and the electrolyte salt. By this measure, it is possible to impart to the fire-retardant gel electrolyte a good ionic conductivity which cannot be obtained by the use of the non-aqueous electrolyte solution only. For instance, the production of a cell having a high resistance to an elevated temperature can be realized.

Further, when the electrolyte salt is  $\text{LiPF}_6$ , the lithium salt may be suitably used in a concentration of 0.4 to 2 M, namely 0.4 to 2 moles per one liter of the non-aqueous solvent. When the concentration of the electrolyte salt to the non-aqueous solvent is lower than 0.4 M, an ionic conductivity of the gel electrolyte is insufficient. On the other hand, when the concentration of the electrolyte salt to the non-aqueous solvent is higher than 2 M, the electrolyte salt is difficult to be dissolved in the non-aqueous solvent. Further, a viscosity of the gel electrolyte as a whole increases so that an ionic conductivity of the gel electrolyte is extremely lowered.

Incidentally, electrolyte materials using the polymer having a side chain to which a nitrile group is bonded have been also proposed in Japanese patent laid-open publication No. 253316/92, Japanese patent laid-open publication No. 271774/94 and Japanese patent laid-open publication No. 279647/94.

However, the electrolyte material disclosed in Japanese patent laid-open publication No. 253316/92, is made of a solid polymer membrane composed primarily of polyacrylonitrile in which lithium ions are contained. This electrolyte material has been suggested to be used particularly as a material for a capacitor. Therefore, the electrolyte material is designed to achieve an improvement in an impedance frequency characteristic thereof. Accordingly, there is no concrete description with respect to improvement in a fire-retardant property and an ionic conductivity of the electrolyte material. The feature of the electrolyte material disclosed in Japanese patent laid-open publication No. 253316/92 rather resides in obtaining a low ionic conductive material.

Further, the electrolyte materials disclosed in Japanese patent laid-open publications Nos. 271774/94 and 279647/94 are composed only of the polymer having a side chain to which a nitrile group is bonded and an salt of alkali metal. As a result, the electrolyte materials disclosed therein are a completely-solid state electrolyte which is not impregnated with any non-aqueous solvent. It is contemplated that the electrolyte material is applied to an electrolyte for a cell to improve its ionic conductivity. However, the ionic conductivity thereof is in a low level, namely merely in the range of  $10^{-6}$  to  $10^{-5}$  S/cm which is not satisfactorily large.

To the contrary, as mentioned above, the fire-retardant gel electrolyte proposed by the present invention is obtained by gelling a non-aqueous electrolyte solution composed of an non-aqueous solvent and an electrolyte salt by using a gelling agent, for example a polymer having a side chain to which at least one nitrile group is bonded. The gel electrolyte can exhibit a high fire retardant property and an enhanced ionic conductivity of 1 mS/cm or higher. That is, the fire-retardant gel electrolyte according to the present invention is different in constituents thereof from the electrolyte materials disclosed in the above-mentioned three Japanese patent laid-open publications. As a consequence, when applied to the production of a cell, the resultant cell using the fire-retardant gel electrolyte according to the present invention



can show an extremely excellent effect or function as compared with those disclosed in the three Japanese patent laid-open publications.

As mentioned above, the thus obtained fire-retardant gel electrolyte can be applied as, for example, an electrolyte material for a cell in a suitable manner. In this case, a cell to which the fire-retardant gel electrolyte according to the present invention is applied may be a primary cell or a secondary cell. When the fire-retardant gel electrolyte is applied to the production of the secondary cell, a positive electrode activating ingredient and a negative electrode activating ingredient used therein may be those enumerated below.

That is, examples of the suitable positive electrode activating ingredient may include a lithium-containing compound, for example, a lithium/transition metal composite oxide represented by a general formula of  $\text{Li}_x\text{MO}_2$  wherein M is at least one transition metal, preferably at least one element selected from the group consisting of Mn, Co and Ni, and x is a number not less than 0.05 but not greater than 1.10.

Whereas, examples of the suitable negative electrode activating ingredient may include metallic lithium, a lithium alloy and a carbonaceous material capable of occluding lithium. Examples of such a carbonaceous material may include pyrolytic carbon, cokes such as pitch cokes, needle cokes and petroleum cokes, graphite, glass-like carbon, a burned product of an organic polymeric compound, which may be obtained by carbonizing and calcining a furan resin or the like at an appropriate temperature, carbon fibers, active carbon, or the like.

Examples:

The present invention is described in more detail by way of examples below.

The fire-retardant gel electrolyte according to the present invention can be obtained by gelling a non-aqueous electrolyte solution, and particularly has a high fire retardant property and an enhanced ionic conductivity of 1 mS/cm or greater at a temperature of 25° C. First, a suitable composition for the fire-retardant gel electrolyte, which can meet the above-mentioned requirements, was investigated as follows.

#### Study on Proportions of Non-Aqueous Solvent and Gelling Agent

A fire-retardant gel electrolyte was prepared in the following manner.

Polyacrylonitrile, ethylene carbonate (EC) and propylene carbonate (PC) were weighed respectively in such amounts as represented in Tables 1 and 2 below. Of those constituents, ethylene carbonate (EC) and propylene carbonate (PC) serving as components of the non-aqueous solvent were first charged into a beaker while agitating to obtain a mixture thereof. Incidentally, the amount (mixing ratio) of polyacrylonitrile shown in Tables was represented in terms of a molar ratio of a monomer as a repeating unit of polyacrylonitrile. The thus obtained mixture was blended with a  $\text{LiPF}_6$  solution having a molar concentration of 1.0 M and the resultant mixture solution was heated to a temperature of 130° C. After the mixture solution was sufficiently subjected to the heating, polyacrylonitrile as a gelling agent was charged slowly into the mixture solution. After completion of the addition of polyacrylonitrile, the mixture solution was heated for 10 minutes while agitating. As a result, a transparent viscous liquid (gel solution) was obtained. The gel solution was then stretched over a glass dish and cooled at room temperature to obtain the aimed fire-retardant gel electrolyte.

The thus obtained gel electrolyte was subjected to the measurement of ionic conductivities ( $\sigma_1$ ,  $\sigma_2$ ) at temperatures of 25° C and -20° C, respectively. The gel electrolyte was further evaluated with respect to a fire retardant property thereof. Methods and procedures used for the measurement of the ion conductivity and the evaluation of the fire retardant property are described below.

#### Measurement of Ion Conductivity

The gel electrolyte prepared above was cut into a cylindrical shape having a diameter of 1 cm. The cylindrical gel electrolyte was interposed between a pair of disc-like platinum electrodes each having a diameter of 1 cm. While maintaining this state, an ionic conductivity of the gel electrolyte was measured by using an impedance analyzer. The measurement was performed under an applied voltage of 0.5 mV and a sweep frequency ranging from 5 MHz to 13 MHz.

#### Evaluation of Fire Retardant Property

500 milligrams of the gel electrolyte 13 prepared above was placed on a filter paper 12 having a size of 10 cm x 10 cm x 0.01 cm, as shown in Fig. 2. The filter paper 12 carrying the gel electrolyte was supported on a supporting block 14 such that an end portion of the filter paper 12 opposite the side where the gel electrolyte was carried, was projected from one end of the supporting block. The projected end portion of the filter paper was directly exposed to a flame of a gas lighter 11 which was placed under the projected portion of the filter paper 12. After the exposure to the flame of the gas lighter 11 was continued for 1 minute, the gas lighter 11 was removed from the position under the filter paper 12. A

portion of the filter paper 12 on which the gel electrolyte was carried was observed about whether or not any burned portion existed. In the event that any burned portion was not observed or burning of the portion was self-extinguished, the conditions were recorded as "not burning" in Tables 1 and 2.

The results of the measurement are shown in Tables 1 and 2 along with the mixing ratio of the respective components of the gel electrolyte.

Table 1

Ex. No. (1)	ANM <sup>(2)</sup> (mol%)	EC <sup>(3)</sup> (mol%)	PC <sup>(4)</sup> (mol%)	IC <sup>(5)</sup>	IC <sup>(6)</sup>	Burning Test	Others (7)
1	5	85	10	4.7	0.4	not burned	-
2	20	70	10	3.6	0.3	not burned	-
3	25	65	10	2.5	0.2	not burned	-
4	5	90	5	4.0	0.03	not burned	-
5	20	75	5	3.5	0.03	not burned	-
6	25	70	5	2.5	0.02	not burned	-
7	5	20	75	3.8	0.4	not burned	-
8	20	20	60	3.4	0.3	not burned	-
9	25	20	55	2.5	0.2	not burned	-

Note:

(1): Experimental Example Number;

(2): Acrylonitrile monomer;

(3): Ethylene carbonate;

(4): Propylene carbonate;

(5): Ionic conductivity  $\sigma_1$  (mS/cm) measured at 25° C;

(6): Ionic conductivity  $\sigma_2$  (mS/cm) measured at -20° C; and

(7): Problems occurring upon the gel formation.

Table 2

Ex.No. (1)	ANM <sup>(2)</sup> (mol%)	EC <sup>(3)</sup> (mol%)	PC <sup>(4)</sup> (mol%)	IC <sup>(5)</sup>	IC <sup>(6)</sup>	Burning Test	Others (7)
10	5	10	85	2.1	0.4	not burned	-
11	20	10	70	1.8	0.4	not burned	-
12	25	10	65	1.1	0.2	not burned	-
13	5	70	25	3.8	0.4	not burned	-
14	20	70	10	2.9	0.4	not burned	-
15	25	70	5	2.2	0.3	not burned	-
16	2	60	38	-	-	not burned	(8)
17	4	60	36	-	-	not burned	(9)
18	30	60	10	1.4	0.1	not burned	(10)

Note:

(1): Experimental Example Number;

(2): Acrylonitrile monomer;

(3): Ethylene carbonate;

(4): Propylene carbonate;

(5): Ionic conductivity  $\sigma_1$  (mS/cm) measured at 25° C;

(6): Ionic conductivity  $\sigma_2$  (mS/cm) measured at -20° C; and

(7): Problems occurring upon the gel formation;

(8): Difficulty in gelation was observed;

(9): Difficulty in gelation was observed;

(10): Slight difficulty in film formation was observed.

On the basis of the results of the measurement shown in Tables 1 and 2, the content of polyacrylonitrile in terms of the acrylonitrile monomer was first investigated. In Experimental Examples 16 and 17 in which small contents of the acrylonitrile polymer, namely 2 mole % and 4 mole %, was used, the gelation of the raw mixture solution was unlikely to proceed smoothly so that extreme difficulty was observed upon production of the gel electrolyte and the measurement of the conductivity thereof was impossible. From this results mentioned above, it was confirmed that the content of the acrylonitrile monomer contained in the gel electrolyte was required to be 5 mole % or greater. On the other hand, when the content of the acrylonitrile monomer contained in the gel electrolyte was as high as 30 mole % as in Experimental Example 18, a viscosity of the raw mixture solution upon the gelation step became too high so that a film formation of the gel electrolyte was relatively difficult. Further increased content of the acrylonitrile monomer contained in the gel electrolyte made it more difficult to achieve a good film formation of the gel electrolyte. From this results, it was determined that an upper limit of the content of the acrylonitrile monomer was 30 mole %.

Next, an investigation was made with respect to a content of propylene carbonate (PC). The gel electrolytes of Experimental Examples 4 to 6 each having a propylene carbonate (PC) content of 5 mole %, exhibited a low ionic conductivity  $\sigma_2$  as compared with those of Experimental Examples 1 to 3 each having a propylene carbonate (PC) content of 10 mole %. Particularly, the ionic conductivity of each of the gel electrolytes of Experimental Examples 4 to 6 was extremely low under a low temperature condition, which was about one-tenth of the ionic conductivities obtained from those of Experimental Examples 1 to 3. From the results mentioned above, it was confirmed that the content of propylene carbonate (PC) contained in the gel electrolyte was required to be 10 mole % or greater.

Further investigation was made with respect to a content of ethylene carbonate (EC). The gel electrolytes of Experimental Examples 10 to 12 each having an ethylene carbonate (EC) content of 10 mole %, exhibited a relatively low ionic conductivity under a temperature of 25° C as compared with those of Experimental Examples 7 to 9 each having an ethylene carbonate (EC) content of 20 mole %. From the results mentioned above, it was confirmed that the content of ethylene carbonate (EC) contained in the gel electrolyte was suitably 20 mole % or greater.

That is, when polyacrylonitrile was used as a gelling agent and a mixture of propylene carbonate (PC) and ethylene carbonate (EC) was used as a non-aqueous solvent, it was confirmed that the contents (mixing ratio) of the respective components were adjusted so as to be fallen within the region surrounded and defined by four sites A, B, C and D of

the ternary composition diagram as shown in Fig. 1 so that the gel electrolyte suitable as an electrolyte for a cell was able to be obtained.

Incidentally, in order to ascertain the above-mentioned results, still further investigation was made, in which the gel electrolyte was prepared such that the contents (mixing ratio) of the respective components were optionally selected from those fallen within or out of the region surrounded by the four sites A, B, C and D. The thus prepared gel electrolytes were subjected to the measurements concerning an ionic conductivity and a fire retardant property. The results of the measurement are shown in Table 3.

Table 3

Ex. No. (1)	ANM <sup>(2)</sup> (mol%)	EC <sup>(3)</sup> (mol%)	PC <sup>(4)</sup> (mol%)	IC <sup>(5)</sup>	IC <sup>(6)</sup>	Burning Test	Others (7)
19*	20	69	11	3.8	0.3	not burned	-
20*	19	55	26	3.0	0.3	not burned	-
21*	19	39	41	2.9	0.3	not burned	-
22*	19	29	52	3.1	0.3	not burned	-
23*	15	57	28	3.0	0.4	not burned	-
24*	13	58	29	3.0	0.3	not burned	-
25*	18	54	27	3.1	0.4	not burned	-
26*	21	56	21	3.0	0.3	not burned	-
27**	18	76	7	3.5	0.01	not burned	-
28**	21	11	68	2.0	0.3	not burned	(8)
29**	18	11	71	2.1	0.3	not burned	(9)
30**	22	0	78	2.0	0.3	not burned	(10)

Note:

(1): Experimental Example Number;

(2): Acrylonitrile monomer;

(3): Ethylene carbonate;

(4): Propylene carbonate;

(5): Ionic conductivity  $\sigma_1$  (mS/cm) measured at 25° C;

(6): Ionic conductivity  $\sigma_2$  (mS/cm) measured at -20° C; and

(7): Problems occurring upon the gel formation;

(8): Difficulty in film formation was observed;

(9): Difficulty in film formation was observed;

(10): Difficulty in film formation was observed.

(\*): The contents of the respective components used in the Experimental Examples 19 through 26 indicated by (\*), were fallen within the region surrounded by the points A, B, C and D of the ternary composition diagram as shown in Fig. 1.

(\*\*): The contents of the respective components used in the Experimental Examples 27 through 30 indicated by (\*\*), were fallen out of the region surrounded by the points A, B, C and D of the ternary composition diagram as shown in Fig. 1.

As understood from the above-mentioned results, it was confirmed that the gel electrolytes, in which the contents of the respective components were fallen within the above-mentioned region of the ternary composition diagram, exhibited a high ionic conductivity and an enhanced fire retardant property. On the other hand, the gel electrolytes in which the content of the respective components were fallen out of the above-mentioned region, showed deficiencies such as difficulty in the film formation and lowering of the ionic conductivity. From the results mentioned above, it was ascertained that, when the contents of the respective components were fallen within the region surrounded by the four sites A, B, C and D of the ternary composition diagram, the suitable gel electrolytes were obtained.

#### Study on Salt of Electrolyte

The gel electrolyte was prepared in the same manner as described above except that the contents of the respective components were fixed such that the ratio of the acrylonitrile monomer: ethylene carbonate (EC): propylene carbonate (PC) was 20 mole %: 60 mole %: 20 mole %, and the lithium salts shown in Fig. 4 were used as the electrolyte salt.

The thus prepared gel electrolytes were subjected to evaluation tests for determining a fire retardant property thereof. The results of the evaluation tests are shown in Table 4.

Table 4

Ex. No. (1)	ANM <sup>(2)</sup> (mol%)	EC <sup>(3)</sup> (mol%)	PC <sup>(4)</sup> (mol%)	Salt of Electrolyte	Burning Test
31	20	60	20	LiPF <sub>6</sub>	not burned
32	20	60	20	LiClO <sub>4</sub>	burned
33	20	60	20	LiBF <sub>4</sub>	burned
34	20	60	20	LiCF <sub>3</sub> SO <sub>3</sub>	burned
35	20	60	20	LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	burned

Note:

(1): Experimental Example Number;

(2): Acrylonitrile monomer;

(3): Ethylene carbonate;

(4): Propylene carbonate.

As shown in Fig. 4, only the gel electrolyte containing LiPF<sub>6</sub> as the electrolyte salt (Experimental Example 31) exhibited a good fire retardant property while the gel electrolytes containing other electrolyte salts was burned. This revealed that LiPF<sub>6</sub> was suitable as the electrolyte salt for the production of fire-retardant cells.

Next, the gel electrolytes were prepared in the same manner as described above except that the ratio of the acrylonitrile monomer: ethylene carbonate (EC): propylene carbonate (PC) was fixed to 20 mole %: 60 mole %: 20 mole %, and LiPF<sub>6</sub> was used in amounts (concentrations) as mentioned in Table 5 to obtain the gel electrolyte.

The thus prepared gel electrolytes were subjected to the measurement of ionic conductivities ( $\sigma$ ) at a temperature of 25° C. The gel electrolytes were also evaluated with respect to their fire retardant property. The results of the measurement and the evaluations are shown in Fig. 5.

Table 5

Ex. No. (1)	ANM <sup>(2)</sup> (mol%)	EC <sup>(3)</sup> (mol%)	PC <sup>(4)</sup> (mol%)	Conc. of SE <sup>(5)</sup>	IC <sup>(6)</sup> (mS/cm)	Burning Test
36	20	60	20	0.3	1.6	not burned
37	20	60	20	0.4	2.0	not burned
38	20	60	20	2.0	3.1	not burned
39	20	60	20	2.1	1.7	not burned

Note:

(1): Experimental Example Number;

(2): Acrylonitrile monomer;

(3): Ethylene carbonate;

(4): Propylene carbonate;

(5): Molar concentration (M) of salt of electrolyte per 1 liter of the non-aqueous solvent (EC plus PC); and

(6): Ionic conductivity  $\sigma$  measured at 25° C.

As is apparent from Table 5, when the concentration of  $\text{LiPF}_6$  on the basis of the non-aqueous solvent was in the range of 0.4 to 2.0 M, the gel electrolyte exhibited a relatively large ionic conductivity of 2.0 or greater. On the other hand, when the concentration of  $\text{LiPF}_6$  on the basis of the non-aqueous solvent was out of the above-mentioned range, the gel electrolyte was less than 2.0. This revealed that a suitable concentration of  $\text{LiPF}_6$  on the basis of the non-aqueous solvent was in the range of 0.4 to 2.0 M.

#### Evaluation of Gel Electrolyte as an Electrolyte Material for Cells

Primary and secondary cells were prepared by using the gel electrolytes as an electrolyte material to evaluate characteristics of the gel electrolyte. Meanwhile, the prepared primary and secondary cells both were of a thin-thickness type as shown in Fig. 3.

First, the thin-thickness type primary cell was prepared in the following manner.

85 % by weight of manganese dioxide (positive electrode activating material), 10 % by weight of graphite and 5 % by weight of polyvinylidene-fluoride were blended with each other. The obtained mixture was further blended with dimethyl-formamide (DMF) as a solvent to prepare a positive electrode preparation. The resultant positive electrode preparation was coated on an aluminum thin film serving as a current collector of the cell. The coated aluminum thin film was dried at a temperature of 120° C under a reduced pressure and then cut into a sheet piece having an surface area of 8 cm<sup>2</sup> to obtain a positive electrode 1.

A negative electrode 2 was prepared by cutting a metallic lithium plate having a thickness of 2 mm into a sheet piece having an surface area of 8 cm<sup>2</sup>.

The thus produced positive and negative electrodes 1 and 2 were received in positive and negative sheathing members 3 and 4, respectively. The positive and negative sheathing members 3 and 4 were laminated in such manner that positive and negative electrodes 1 and 2 received therein were opposed to each other.

The gel electrolyte layer 6 was prepared in the following manner.

The gel solution was prepared from polyacrylonitrile, ethylene carbonate (EC), propylene carbonate (PC) and  $\text{LiPF}_6$ . The thus prepared gel solution was immediately stretched on one side surface of a separator film 5 and then cooled at room temperature to form a gel electrolyte layer 6 having a thickness of 120  $\mu\text{m}$  thereon. A similar gel electrolyte layer 6 was also formed on the other side surface of the separator film 5. Incidentally, the ratio of the respective components in the gel solution was as follows. Namely, the gel solution contained 15 mole % of the acrylonitrile monomer, 57 mole % of ethylene carbonate (EC), 28 mole % of propylene carbonate (PC) and 0.8 M of  $\text{LiPF}_6$  (on the basis of a total amount of the non-aqueous solvent components). A non-woven fabric having a thickness of about 20  $\mu\text{m}$  was employed as the separator film 5.

The separator film 5 on which the gel electrolyte layer 6 was coated was interposed between the laminated positive and negative electrodes 1 and 2. The positive and negative sheathing members 3 and 4 were heat-fused and sealed at outer peripheral flanges through a hot-melt adhesive material 7 to form the thin-thickness type primary cell.

The thus prepared primary cell was examined with respect to its discharging characteristics.

The discharge used for the above examination was a constant-current discharge, which was carried out at a current density of 200  $\mu\text{A}/\text{cm}^2$  and continued until a voltage of the open circuit reached 1.8 volts. The measured discharging characteristic curve was illustrated in Fig. 4.

As understood from Fig. 4, an average voltage of the primary cell upon discharging was about 2.8 volts and the voltage curve exhibited a good flatness, by which it was recognized that the gel electrolyte employed were suitably used as an electrolyte material for primary cells.

Next, a thin-thickness type secondary cell was prepared in the following manner. Incidentally, the same procedure as described in the production of the primary cell above was repeated to prepare the secondary cell except that lithium cobaltate was used as the positive electrode activating material.

The thus prepared secondary cell was tested to determine charging and discharging characteristics thereof.

The charging and discharging tests were carried out as follows. Namely, a constant-current charge was carried out at a current density of  $25 \mu\text{A}/\text{cm}^2$  and continued until a voltage of the open circuit reached 4.2 volts, upon which the constant-current charge was changed over to a constant-voltage charge. The constant-voltage charge was continued until a total charging time reached 20 hours. Thereafter, a constant-current discharge was carried out at a current density of  $200 \mu\text{A}/\text{cm}^2$  until a voltage of the open circuit reached 2.5 volts. The above-mentioned charging and discharging cycle was repeated several times. Charging and discharging characteristic curves for the second and fifth charging and discharging cycles are shown in Fig. 5.

As understood from Fig. 5, it was confirmed that charging and discharging efficiencies of the secondary cell were 90 % or higher at both the second and fifth charging and discharging cycles. This revealed that the gel electrolyte is suitably and satisfactorily employed as an electrolyte material for secondary cells.

As mentioned above, the gel electrolyte according to the present invention exhibits a fire-retardant property and an ionic conductivity of 1 mS/cm or greater at a temperature of  $25^\circ\text{C}$  so that the gel electrolyte can be used as an electrolyte material for cells.

By using such a gel electrolyte as an electrolyte material, a cell has an excellent safety due to its fire-retardant property, for instance, even when it is exposed to the flame. Further, the cell containing such a gel electrolyte does not cause any leakage of electrolyte even when handled roughly so that contamination of devices to which the cell is mounted can be effectively prevented.

## Claims

1. A fire-retardant gel electrolyte comprising a gelled solution composed of a non-aqueous solvent and a salt of an electrolyte dissolved in said non-aqueous solvent, said gel electrolyte having an ionic conductivity of 1 mS/cm at a temperature of  $25^\circ\text{C}$ .
2. The fire-retardant gel electrolyte according to claim 1, wherein the gelation of a solution containing said non-aqueous solvent and said electrolyte salt dissolved in said non-aqueous solvent is carried out by adding a polymer having a side chain to which at least one nitrile group is bonded.
3. The fire-retardant gel electrolyte according to claim 2, wherein said polymer having a side chain to which at least one nitrile group is bonded is polyacrylonitrile.
4. The fire-retardant gel electrolyte according to claim 3, wherein said polymer having a side chain to which at least one nitrile group is bonded is polyacrylonitrile, and a ratio of said polyacrylonitrile in terms of an acrylonitrile monomer to said non-aqueous solvent is in the range of 5:95 to 30:70.
5. The fire-retardant gel electrolyte according to claim 1, wherein said non-aqueous solvent constituting said gelled solution contains at least one compound selected from the group consisting of ethylene carbonate, propylene carbonate,  $\gamma$ -butyl-lactone, methyl-ethyl carbonate and dimethyl carbonate.
6. The fire-retardant gel electrolyte according to claim 5, wherein said non-aqueous solvent constituting said gelled solution contains at least one compound selected from the group consisting of ethylene carbonate and propylene carbonate.
7. The fire-retardant gel electrolyte according to claim 6, wherein said polymer having a side chain to which at least one nitrile group is bonded is polyacrylonitrile, said non-aqueous solvent constituting said gelled solution is a mixture of ethylene carbonate and propylene carbonate, and a ratio of polyacrylonitrile in terms of the acrylonitrile monomer: ethylene carbonate: propylene carbonate is fallen within a region surrounded and defined by A site (the acrylonitrile monomer: 30 mol %, ethylene carbonate: 20 mol %, propylene carbonate: 50 mol %), B site (the acrylonitrile monomer: 5 mol %, ethylene carbonate: 20 mol %, propylene carbonate: 75 mol %), C site (the acrylonitrile monomer: 5 mol %, ethylene carbonate: 85 mol %, propylene carbonate: 10 mol %) and D site (the acrylonitrile monomer: 30 mol %, ethylene carbonate: 60 mol %, propylene carbonate: 10 mol %) of ternary composition diagram.

8. The fire-retardant gel electrolyte according to claim 1, wherein said electrolyte salt of the gelled solution is  $\text{LiPF}_6$  and  $\text{LiPF}_6$  is contained in said gelled solution in an amount of 0.4 to 2 mole per one liter of said non-aqueous solvent.

5 9. A cell comprising:

a fire-retardant gel electrolyte having an ionic conductivity of 1 mS/cm or greater at a temperature of 25° C;

and

positive and negative electrodes.

10 10. The cell according to claim 9, wherein said positive electrode is made of a lithium-containing compound and said negative electrode is made of a material selected from the group consisting of metallic lithium, a lithium alloy and a carbonaceous material capable of occluding lithium.

11. The cell according to claim 10, wherein said lithium compound constituting said positive electrode is a composite  
15 oxide of lithium and a transition metal.

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	ACRYLONITRILE MONOMER (mol%)	EC (mol%)	PC (mol%)
A	30	20	50
B	5	20	75
C	5	85	10
D	30	60	10

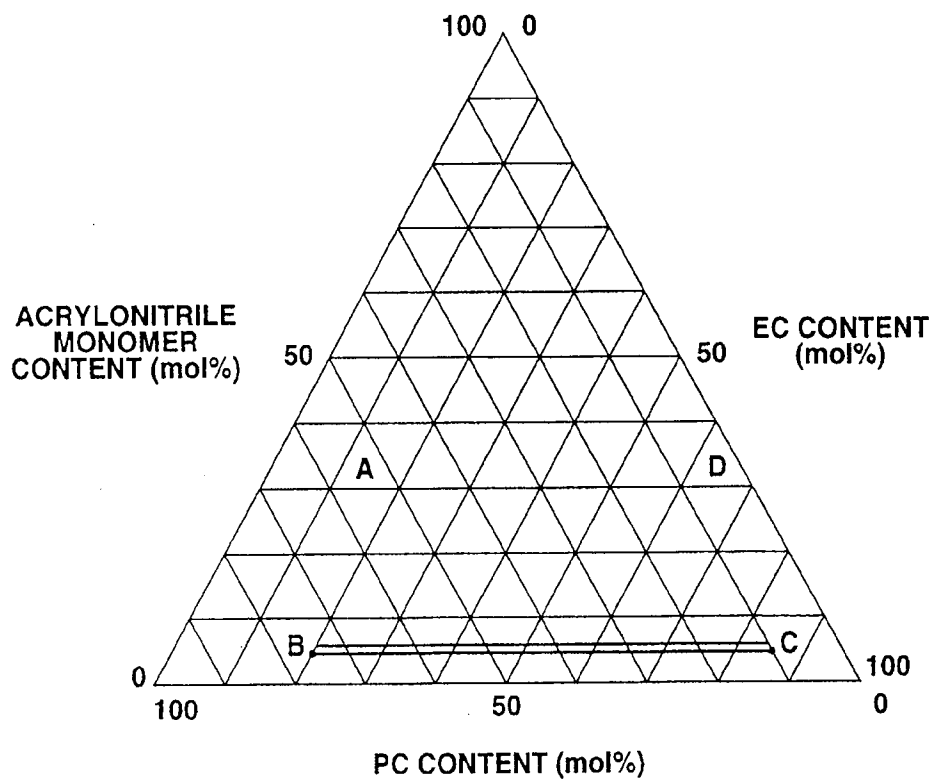


FIG.1

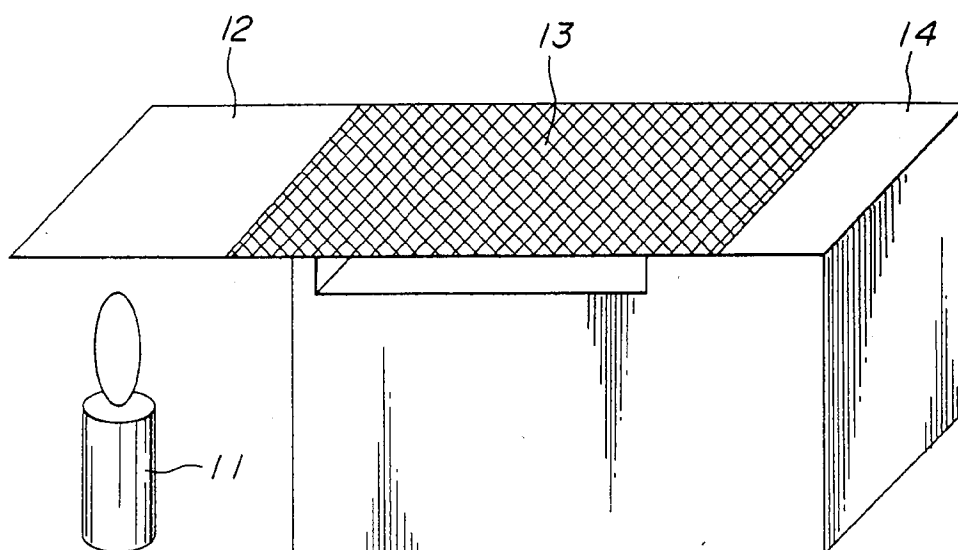


FIG.2

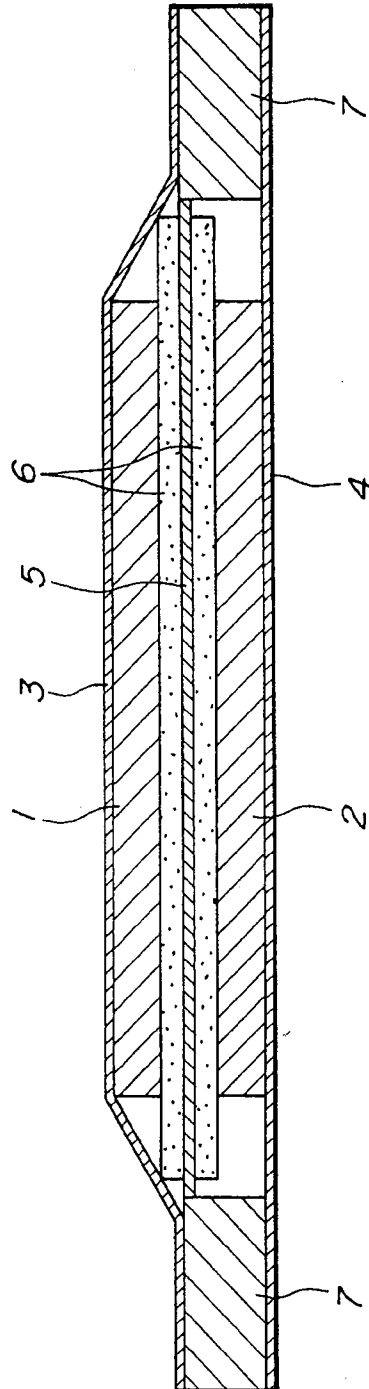
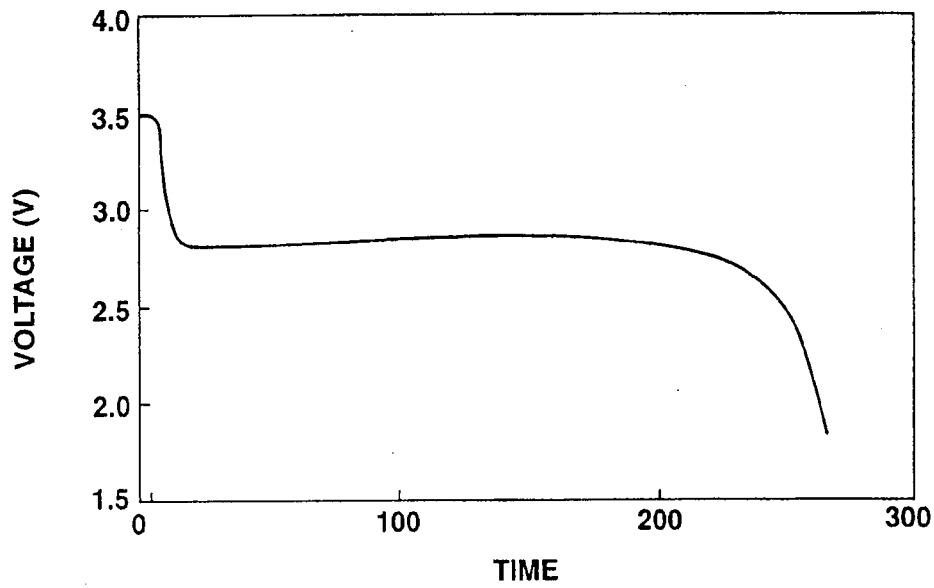
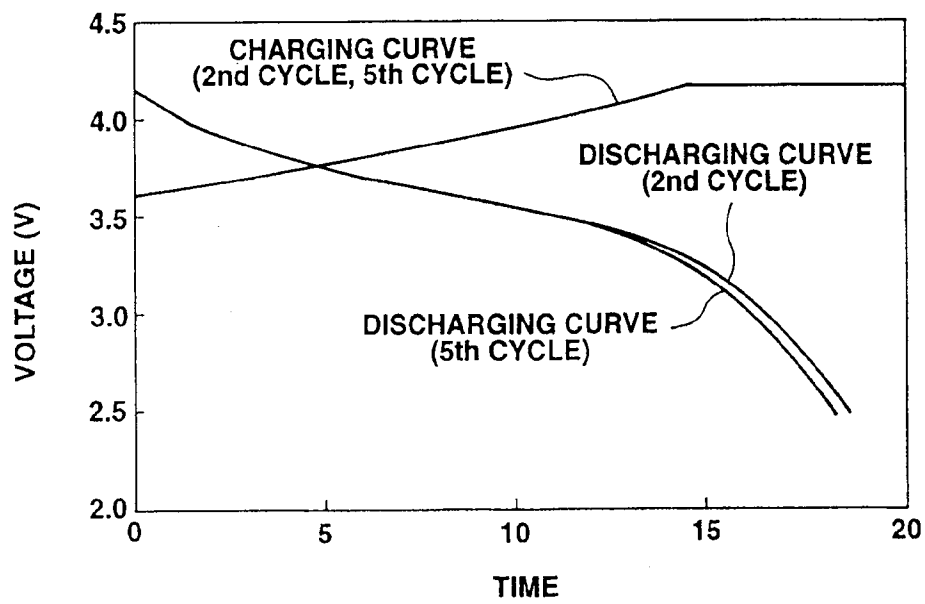


FIG.3



**FIG. 4**



**FIG. 5**



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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 10 0931

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 80 (E-590), 12 March 1988 & JP-A-62 219469 (HITACHI MAXELL LTD) * abstract *	1-4,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 April 1996	Examiner De Vos, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 April 1996	Examiner De Vos, L
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>..... &amp; : member of the same patent family, corresponding document</p>			